3.2.2 Sample Containers, Preservation Technologies, Holding Times

Sample containers, preservation techniques and holding times will be as shown in Table 1 of this document. This table has been modified from one included in Exhibit C of US EPA Region II CERCLA Quality Assurance Manual (Reference 3). The revisions are the deletion of Dioxin, the increase of holding time for aqueous extractable organics to 7 days to allow for shipping from Puerto Rico to North Carolina, the preservation of soil samples at 4°C (cool), and the decrease of holding time for volatile organics in soil to 7 days. The validity of samples which exceed the goals by any length of time will be determined by the Radian and prime contractor (Golder) chemists in conjunction with US EPA Region II on a case by case basis.

Sample containers will be cleaned to 300 series specifications. It may be necessary to rinse the outer portion of sample containers with deionized water prior to packaging for shipment. The latest Department of Transportation procedures for shipment of environmental samples will be used in all cases. The quantity of acids or bases added as preservatives will not exceed 0.15 percent by weight and the samples will not be shipped as corrosives.

3.2.3 Sampling Blanks and Duplicates

- Trip blanks will be 40 ml VOA vials with Teflon septa lids. The vials will be filled with analyte-free or HPLC grade water at the laboratory and accompany the bottles from the laboratory, into the field and back to the laboratory. Trip blanks will be taken when aqueous samples are analyzed for volatiles. The trip blanks will be taken at a frequency of one per day per aqueous matrix ~~or one per shipment~~, whichever is more frequent. Trip blanks will be analyzed for the volatile organic compounds for which investigative samples are being analyzed at a frequency of at least one per aqueous matrix per week or per sampling event, whichever frequency is greater.

3.0 RADIAN LABORATORY QA PROGRAM PLAN

3.1 Scope of Plan

The Radian Plan (Appendix A), when read in conjunction with Section 3 of this document and the CLP SOW's (References 1 and 2) provide for field instrument maintenance/calibration and laboratory QA for all aspects of the work. In addition, the production of analyte-free water is described in an SOP included at the back of the Radian QA plan. Due to confidentiality reasons, only parts of this procedure have been reproduced. The whole procedure will be made available to EPA on request. This section describes how the Radian Plan is used for the two QA programs.

3.2 RFA QA

The Radian Plan, in conjunction with the letter from Radian dated July 29, 1988 (included in Appendix A), the CLP SOW's (References 1 and 2) and the following constitute the RFA/QA. The requirements of the CLP SOW take precedence over the Radian Plan.

3.2.1 Applicability and Methodologies

The RFA QA will apply to all soil samples (see References 6 and 7) obtained for the RFA and the baseline monitoring sampling for the Priority Pollutant parameters, plus 40 peaks listed in Appendix A of the Groundwater Monitoring Plan (see Reference 8). Analysis will be by CLP methodologies. Those analytes which are not on the TCL/TAL lists are amenable to CLP procedures.

2.3.12 Preventative Maintenance

Field and laboratory equipment preventative maintenance is included in Section 11.0 of the ESE Plan. Golder Associates may use these methods for field equipment but expect to use the methods listed in Appendix E.

2.3.13 Miscellaneous

Procedures used to assess data precision, accuracy and completeness and QA corrective action protocols are noted in Sections 12.0 and 13.0 of the ESE Plan. Responsibility to carry out these procedures will rest with ESE for laboratory tasks and with the prime contractor for field related tasks. The prime contractor (Golder) will also provide overview of all the elements of the QA Plan.

2.3.9 Data Reduction, Validation and Reporting

The standard deliverable that is required from the laboratory will contain the sample number, laboratory sample identification number, result, unit, detection limit, and the appropriate laboratory qualifiers. Section 8.0 of the ESE Plan governs the internal laboratory work for the MQA. All potential analytical problems will be discussed with the prime contractor (Golder) and a narrative will be sent to US EPA as appropriate. Data will be transferred from the laboratory to the prime contractor (Golder) by disk where it will be incorporated into a relational and/or flat file database. The data will be reported to US EPA in tabular form with a narrative discussing the complete sampling and analysis event. Further information is included in Sections 8.0, 9.0 and 10.0 of the Groundwater Monitoring Plan (Reference 8).

2.3.10 Internal Quality Control Checks

The internal QC checks which will be used by ESE to perform the MQA analysis are discussed in Section 9.0 of the ESE Plan.

2.3.11 Performance and Systems Audits

Section 10.0 of the ESE plan discusses performance and system audits. The prime contractor (Golder) will be responsible for field operations and office work within their offices. ESE will be responsible for laboratory operations and office work within ESE. When Section 10.0 is read, the references to QA Supervisor must be considered to apply to ESE and the references to prime contractor must be considered to apply to Golder. Overall responsibility for QA remains with the prime contractor (Golder).

2.3.5 Sample Container Cleaning Procedures

The sample containers will be cleaned as noted in Table 4.2 and paragraph 4.5.1 of the ESE Plan.

2.3.6 Sample Custody

The field custody procedures are noted in the Groundwater Monitoring Plan (Reference 8). The chain-of-custody form to be used is that produced by US EPA Region II and is included in Appendix C.

Laboratory sample custody and documentation is detailed in Sections 5.2 and 5.4 of the ESE Plan.

2.3.7 Calibration Controls and Frequency

Section 6.0 of the ESE Plan addresses field and laboratory instrument calibration. Minor modification of this section has been performed by Golder Associates to allow for the actual field instruments to be used and the removal of reference to procedures which are definitely outside the scope of the project. The calibration of the Hach one pH meter is included in Appendix D.

2.3.8 Analytical Procedures

Section 7.0 of the ESE Plan allows for many different analytical procedures. Table 2 lists the preferred analytical methods for each parameter. Any deviation from the original method will be documented and a narrative discussing the ramifications of the change will be forwarded to US EPA in a timely manner.

2.3.3 Sample Containers, Preservation Techniques, Holding Times

Table 4.1 of the ESE Plan lists the containers, preservation techniques and holding times that would be used on water samples analyzed by ESE as part of the MQA.

2.3.4 Sampling Blanks and Duplicates

- Trip blanks will be 40 ml VOA vials with Teflon septa lids. The vials will be filled with analyte-free or HPLC grade water at the laboratory and accompany the bottles from the laboratory, into the field and back to the laboratory. Trip blanks will be taken when aqueous samples are analyzed for volatiles. The trip blanks will be taken at a frequency of one per day per aqueous matrix or one per shipment, whichever is more frequent. Trip blanks will be analyzed for the volatile organic compounds for which investigative samples are being analyzed at a frequency of at least one per aqueous matrix per week or per sampling event, whichever frequency is greater.
- Rinsate blanks will be obtained as specified in the sampling plans.
- One duplicate will be obtained for every sampling event.
- If a resampling is necessary, a sample may be split with another commercial laboratory.
- Splits for use by the US EPA Region II will be obtained as requested.
- Tables 4 and 5 list the types of samples by matrix.
- Table 6 lists additional samples and sampling blanks to be taken during the field program as described in Reference 8.

The above blanks and duplicates are considered adequate for the proposed monitoring system as described in Reference 8. This section will be reviewed and appropriate revisions will be made if any change in the monitoring network is implemented.

2.2.11 Performance and System Audits

Section 10.0 of the ESE plan discusses performance and system audits. The prime contractor (Golder) will be responsible for field operations and office work within their offices. ESE will be responsible for laboratory operations and office work within ESE. When Section 10.0 is read, the references to QA Supervisor must be considered to apply to ESE and the references to prime contractor must be considered to apply to Golder. Overall responsibility for QA remains with the prime contractor (Golder).

2.2.12 Preventative Maintenance

Field and laboratory equipment preventative maintenance is included in Section 11.0 of the ESE Plan. Golder Associates may use these methods for field equipment but expect to use the methods listed in Appendix E.

2.2.13 Miscellaneous

QA will not be run by the batch method, but instead on project specific samples as specified by CLP procedures.

2.3 Monitoring QA (MQA)

2.3.1 Applicability and Methodologies

The MQA will be used for all groundwater monitoring except the baseline monitoring sampling for Priority Pollutants, as described in the Groundwater Monitoring Plan. The methods used will be those stated in Table 2.

2.3.2 Sampling Procedures

The text of Section 4.0 of the ESE Plan which relates to sampling procedures has been removed. Sampling procedures have been discussed in the Groundwater Monitoring Plan (Reference 8).

2.2.8 Analytical Procedures

All analysis will be performed using CLP procedures as stated in the CLP SOW's (Reference 1 and 2). Those analytes which are not included on the TCL/TAL lists are amenable to CLP procedures.

2.2.9 Data Reduction, ~~Validation~~ and Reporting

Deliverables from the laboratory will contain all the elements of a CLP package but will not necessarily be presented on the CLP forms. Data reduction ~~and validation~~ will be in accordance with CLP SOW's and will be reviewed by both ESE and the prime contractor (Golder). ~~Golder will validate the data using US EPA, Laboratory Data Validation, Functional Guidelines for Evaluating Organics Analysis (Reference 4) and US EPA Region II Evaluation of Metals Data for the Contract Laboratory Program (Reference 5), QC summary sheets,~~ Data results and a narrative will be supplied to US EPA Region II. ~~Raw data will not be included.~~

Data will be transferred from the laboratory to the prime contractor (Golder) by diskette where it will be incorporated into a relational and/or flat file database. The data will be reported to US EPA Region II in tabular form with a narrative discussing the complete sampling and analysis event. Further information is included in the soil sampling plans (References 6 and 7) and in the Groundwater Monitoring Plan (Reference 8).

2.2.10 Internal Quality Control Checks

The internal QC checks which will be used by ESE to perform the RFA analysis are discussed in Section 9.0 of the ESE Plan and Exhibit E of the CLP SOW's. The requirements for the CLP SOW take precedence over the ESE Plan.

reviewed and appropriate revisions will be made if any change in the monitoring network or soil sampling events are implemented.

2.2.5 Sample Container Cleaning Procedures

Sample containers will not be cleaned by ESE. All containers for the RFA level of QA will be supplied by I Chem of California and will be of the 300 series.

It may be necessary to rinse the outer portion of sample containers with deionized water prior to packaging for shipment. The latest Department of Transportation procedures for shipment of environmental samples will be used in all cases. The quantity of acids or bases added as preservatives will not exceed 0.15 percent by weight and, therefore, the samples will not be shipped as corrosives.

2.2.6 Sample Custody

The field custody procedures are noted in the RFA soil sampling plans and the Groundwater Monitoring Plan (References 6, 7 and 8). The chain-of-custody form to be used, produced by US EPA Region II, is included in Appendix C. Each shipment containing soil will be accompanied by a United States Department of Agriculture (USDA) permit label, provided by the laboratory. The laboratory permit is included with the QA plan in Appendix B.

2.2.7 Calibration Controls and Frequency

Section 6.0 of the ESE Plan addresses field and laboratory instrument calibration. Minor modification of this section has been performed by Golder to allow for the actual field instruments to be used and the removal of reference to procedures which are definitely outside the scope of the project. The calibration of the Hach one pH meter is included in Appendix D.

shipping from Puerto Rico to Florida, the preservation of soil samples at 4°C (cool) and the decrease of holding time for volatile organics in soil to 7 days. The validity of samples which exceed the goals by any length of time will be determined by the ESE and prime contractor (Golder) chemists in conjunction with US EPA Region II on a case by case basis.

2.2.4 Sampling Blanks and Duplicates

- Trip blanks will be 40 ml VOA vials with Teflon septa lids. The vials will be filled with analyte-free or HPLC grade water at the laboratory and accompany the bottles from the laboratory, into the field and back to the laboratory. Trip blanks will be taken when aqueous samples are analyzed for volatiles. The trip blanks will be taken at a frequency of one per day per aqueous matrix or one per shipment, whichever is more frequent. Trip blanks will be analyzed for the volatile organic compounds for which investigative samples are being analyzed at a frequency of at least one per aqueous matrix per week or per sampling event, whichever frequency is greater.
- Rinsate blanks will be obtained as specified in the sampling plans.
- One duplicate will be obtained per 10 investigative samples.
- If a resampling is necessary a sample may be split with another commercial laboratory.
- Splits for use by the US EPA Region II will be obtained as requested.
- Additional QA samples will be obtained to allow for CLP SOW Matrix Spikes, etc.
- Tables 3, 4, and 5 list the types of samples by matrix.
- Table 6 lists additional samples and sampling blanks to be taken during the field program described in Reference 8.

The above blanks and duplicates are considered adequate for the proposed monitoring system and the proposed soil sampling events (see References 6, 7 and 8). This section will be

2.0 ESE QA PLAN

2.1 Scope of Plan

The modified ESE QA (ESE Plan) (Appendix B), when read in conjunction with Section 2, Appendices D and E of this document and the CLP SOW's (References 1 and 2) provides for field instrument maintenance and laboratory QA for all aspects of the work. In addition, the production of analyte-free water for use as blanks by the laboratory is described in the back of the ESE QA plan. Portions of the RFA/QA and MQA are delineated in the ESE Plan. This section describes how the ESE Plan is used for the two QA programs.

2.2 RFA QA

2.2.1 Applicability and Methodologies

The RFA QA will apply to the analysis of soil samples described in the RFA Work Plans (Reference 6 and 7) and the baseline monitoring for the priority pollutants, plus 40 peaks, as specified in Appendix A of the Groundwater Monitoring Plan (Reference 8).

2.2.2 Sampling Procedures

The text of Section 4.0 of the ESE Plan which relates to sampling procedures has been removed. Sampling procedures have been discussed in the soil sampling plans (References 6 and 7) and in the Groundwater Monitoring Plan (Reference 8).

2.2.3 Sample Containers, Preservation Techniques, Holding Times

Sample containers, preservation techniques and holding times will be as shown in Table 1 of this document. This table has been modified from one included in Exhibit C of US EPA Region II CERCLA Quality Assurance Manual (Reference 3). The revisions are the deletion of Dioxin, the increase of holding time for aqueous extractable organics to 7 days to allow for

After the soil analysis and baseline groundwater analysis has been completed, background groundwater monitoring will commence. During background, detection and compliance groundwater monitoring, and also during the baseline sampling of the wells for non-priority pollutants as specified in Appendix A of the Groundwater Monitoring Plan (Reference 8) following well development, the MQA program will be used.

The main elements of the MQA are: Sample preservation and holding times as summarized in Table 1; analysis by the standard methods incorporated in the ESE or Radian QA Plans and summarized in Table 2; the use of bottles as required by the appropriate method; the production of a standard deliverable package which will include sample number, laboratory sample identification number, result, unit, detection limit and appropriate laboratory qualifiers; data validation by the methodologies required by the appropriate analytical technique together with the ESE/Radian QA Plan and batch QA/QC; Golder Associates Inc. (Golder) will discuss the validation with the laboratory and a summary narrative will be sent to US EPA Region II).

Statements of Work (SOW's) (Reference 1 and 2); EPA Region II, Comprehensive Environmental Response Compensation and Liability Act (CERCLA) Quality Assurance Manual (Reference 3); US EPA, Laboratory Data Validation, Organics (Reference 4); EPA Region II, Evaluation of Metals Data for the CLP Program (Reference 5) and various task specific documents.

1.2 QA Levels

The QA for the various tasks exist at two separate levels depending on the task or on the stage within a task. In general, the laboratory analysis for the RCRA Facility Assessment (RFA) is based on strict QA which is very similar to that used in the CERCLA program. A separate level of QA will be used for long-term groundwater monitoring of the municipal landfill. The field instrument maintenance will remain constant throughout the project.

The RFA QA will apply to the analysis of soil samples described in the RFA Work Plans (References 6 and 7) and the baseline monitoring for the Priority Pollutant parameters (plus 40 peaks) as specified in Appendix A of the Groundwater Monitoring Plan (Reference 8). All non-priority pollutants in the baseline monitoring will be analyzed using the monitoring QA program (MQA).

The main elements of the RFA QA are: Analysis of the above parameters by the latest revision of CLP SOW's including non-batch procedures; the use of 300 series bottles; production of all components of a CLP deliverable package; and, data validation of the CLP package components by EPA Region II specified methods. CLP requirements take precedence over requirements of the ESE plan, Radian plan, and all sampling and analysis plans except the requirements listed in Table 1 (Preservation and Holding Times) and the use of CLP forms will not be required.

1.0 INTRODUCTION

1.1 Scope

This plan should be read in conjunction with the soil sampling plans and the Groundwater Monitoring Plan (References 6, 7 and 8) submitted for the Ponce Municipal Landfill. The groundwater monitoring program for the site, described in the Groundwater Monitoring Plan (Reference 8), includes both groundwater sampling and surface water sampling. Thus, the Groundwater Monitoring Plan sampling protocol referenced in this QA plan is for groundwater sampling and surface water sampling. This plan is restricted to laboratory quality assurance/quality control (QA/QC), field instrument maintenance/calibration and the chain-of-custody form. Discussion of the general network design, specific sample site selection, parameter selection, safety and other task specific issues have been addressed in other submissions (References 6, 7 and 8) to United States Environmental Protection Agency (US EPA Region II or Agency).

This submittal was to have consisted of documents prepared by the laboratories proposed for the project: Environmental Science and Engineering, Inc. (ESE) of Gainesville, Florida and Radian Corporation (Radian) of Research Triangle Park, North Carolina. The documents produced by ESE and Radian meet the usual QA requirements for a project of this type, but do not meet additional QA/QC requirements requested by EPA Region II. This plan describes the modifications and additions to the ESE and Radian plans needed to meet the QA/QC requested by the Agency.

The plan references the following documents: Radian Laboratory Quality Assurance Plan (Appendix A); ESE Quality Assurance Plan, modified by J. Paul, Golder Associates (Appendix B); US EPA Contract Laboratory Program (CLP),

TABLE OF CONTENTS
(CONT'D)

APPENDIX A - Radian Corporation Laboratory Quality Assurance Program Plan
APPENDIX B - Modified ESE QA Plan
APPENDIX C - US EPA Region II Chain-of-Custody Record
APPENDIX D - Calibration of Hach One pH Meter
APPENDIX E - Preventative Maintenance for:
Hach One pH Meter and Temperature Probe
Myron Conductivity Meter

TABLE OF CONTENTS
(CONT'D)

3.0	RADIAN LABORATORY QA PROGRAM PLAN		13
	3.1	Scope of Plan	13
	3.2	RFA QA	13
		3.2.1 Applicable and Methodologies	13
		3.2.2 Sample Containers, Preservation Technologies, Holding Times	13
		3.2.3 Sampling Blanks and Duplicates	14
		3.2.4 Sample Custody	14
		3.2.5 Data Reduction Validation and Reporting	15
		3.2.6 Field Instrument Calibration and Preventative Maintenance	15
		3.2.7 Miscellaneous	16
	3.3	Monitoring QA (MQA)	16
		3.3.1 Applicability and Methodologies ...	16
		3.3.2 Sample Container, Preservative Techniques, Holding Times	17
		3.3.3 Sampling Blanks and Duplicates	17
		3.3.4 Sample Custody	17
		3.3.5 Data Reduction Validation and Reporting	18
		3.3.6 Field Instrument Calibration and Preventative Maintenance	18
REFERENCES			19
			20

In Order Following Page 20

TABLE 1 - Preservation and Holding Time Requirements
TABLE 2 - Proposed Analytical Methods for the Parameters Analyzed at the Ponce Municipal Landfill, Puerto Rico
TABLE 3 - RFA Soil Sampling
TABLE 4 - Groundwater Sampling
TABLE 5 - Surface Water Sampling
TABLE 6 - Miscellaneous QA Sampling

TABLE OF CONTENTS

Cover Letter

Table of Contents i

SECTION			PAGE
1.0	INTRODUCTION		1
	1.1	Scope	1
	1.2	QA Levels	2
2.0	ESE QA PLAN		4
	2.1	Scope of Plan	4
	2.2	RFA QA	4
		2.2.1 Applicability and Methodologies	4
		2.2.2 Sampling Procedures	4
		2.2.3 Sample Containers, Preservation Techniques, Holding Times	4
		2.2.4 Sampling Blanks and Duplicates	5
		2.2.5 Sample Container Cleaning Procedures	6
		2.2.6 Sample Custody	6
		2.2.7 Calibration Controls and Frequency	6
		2.2.8 Analytical Procedures	7
		2.2.9 Data Reduction, Validation and Reporting	7
		2.2.10 Internal Quality Control Checks	7
		2.2.11 Performance and Systems Audits	8
		2.2.12 Preventative Maintenance	8
		2.2.13 Miscellaneous	8
	2.3	Monitoring QA (MQA)	8
		2.3.1 Applicability and Methodologies	8
		2.3.2 Sampling Procedures	8
		2.3.3 Sample Containers, Preservation Techniques, Holding Times	9
		2.3.4 Sampling Blanks and Duplicates	9
		2.3.5 Sample Container Cleaning Procedures	10
		2.3.6 Sample Custody	10
		2.3.7 Calibration Controls and Frequency	10
		2.3.8 Analytical Procedures	10
		2.3.9 Data Reduction, Validation and Reporting	11
		2.3.10 Internal Quality Control Checks	11
		2.3.11 Performance and Systems Audits	11
		2.3.12 Preventative Maintenance	12
		2.3.13 Miscellaneous	12

A STATISTICAL "COOKBOOK" FOR GROUND-WATER MONITORING AT THE BFIP FACILITY

Robert D. Gibbons
University of Illinois

February 26, 1988

ATTACHMENT IV-5

STATISTICAL PROCEDURES

* References and citations made to specific sections, tables, figures or other sources which are not included in this Attachment are available in BFI's revised Post-Closure Permit application, dated May, 1989 and is in the Administrative Record. The Administrative Record is located at U. S. Environmental Protection Agency, Region II, Permits Administration Branch, 26 Federal Plaza, New York, N.Y., 10278 and the Puerto Rico Environmental Quality Board, Santurce, Puerto Rico, 00910-1488.

We appreciate the opportunity to continue assisting BFI with is project.

Very truly yours,

GOLDER ASSOCIATES INC.

W. Randall Sullivan, P.E.
Associate

WRS:rcs

Enclosures

RESPONSE:

Section 1.2 of the Quality Assurance Plan has been amended to indicate the precedence of CLP requirement over the laboratory sampling plans for RFA samples, and all sampling and analysis plans, except the requirements listed in Table 1.

COMMENT:

10. The QA plan references the use of the latest CLP statements of work. The most recent statement of work for organics and inorganics are February 1988 and December 1987, respectively. The list of references on page 18 of the QA plan should be changed to reflect this.

RESPONSE:

The Reference list to the Quality Assurance plan has been amended to include the most recent versions of the CLP statement of work.

COMMENT:

11. Not all of the priority pollutants are CLP target compound list (TCL) analytes. Those which are not TCL analytes are amenable to CLP procedures. We would like the plan to confirm that CLP procedures will be used and to detail any appropriate modifications which will be used.

RESPONSE:

Sections 2.2.8 and 3.2.1 of the Quality Assurance Plan indicate that the parameters that are not present on the TCL/TAL lists are amenable to CLP procedures and will be analyzed using CLP methodologies.

COMMENT:

12. Preservation of filtered metals is not indicated in the QA plan.

RESPONSE:

Table 1 of the Quality Assurance Plan has been amended to include the preservation requirements of filtered metals.

COMMENT:

7. Homogenization of soil samples should be done by the cone and quarter method described on page 55 of the Region II CERCLA Quality Assurance Manual referenced in the QA plan.

RESPONSE:

A response is addressed in the soil sampling plans (References 6 and 7).

COMMENT:

8. Table 1 of the QA plan lists sample container, preservation, and holding time requirements. This table should be changed as follows:

   a. Preservation of soil samples for all analytes should be "cool, 4°C."

   b. The holding for volatile organics in soil should be 7 days.

RESPONSE:

Table 1 and sections 2.2.3 and 3.3.2 of the Quality Assurance Plan have been amended to allow for the stated preservation for soil samples and holding times for soil samples to be analyzed for volatile organics.

COMMENT:

9. Section 1 of the QA plan should state that CLP requirements take precedence over requirements of the ESE plan, Radian plan, and all sampling plans. The exception is that sample container, preservation, and holding time requirements should conform to Table 1 of the QA plan as modified by Comment 8, above.

   An example of CLP requirements taking precedence over requirements of the various plans is as follows. Page 8 of the work plan for cover soil sampling states that 60 ml vials with Teflon lined lids should be used for collecting volatile organic samples. We ask that the 40 ml VOA vials detailed in Table 1 be used rather than these.

to transfer surface water samples to sample containers. This information should be incorporated into all of the appropriate sections and appendices where decontamination procedures are described.

RESPONSE:

A response is addressed in Revision 2 of the soil sampling plans (References 6 and 7) and in Revision 2 of the Groundwater Monitoring Plan (Reference 8).

COMMENT:

5. The frequency of equipment rinsate blanks described in various parts of the QA plan does not appear to be adequate. We ask that one rinsate blank be done for each individual type of equipment each time a decon event occurs. Compositing is not allowed.

RESPONSE:

In a phone discussion with Fred Haber of the EPA on January 12, 1989, it was agreed that one rinsate blank is required to be taken per sampling equipment decontamination event per batch of sampling equipment following decontamination.

The frequency of equipment rinsate blanks has been indicated on Tables 3, 4, and 5 in the QA Plan. However, as noted in the tables, the number of these blanks will depend on the equipment used. The Groundwater Monitoring Plan and soil sampling plans (References 6, 7 and 8) have incorporated procedures used for determining how many equipment rinsate blanks will be used.

COMMENT:

6. Demonstrated analyte free water should be used for all blanks and the method of demonstrating such should be included in the plan.

RESPONSE:

HPLC water or a laboratory demonstrated analyte free water, will be used for all blanks. The Quality Assurance plan includes parts of each laboratory's SOPs for demonstrating that their water is analyte free.

operating procedures for sampling will be used? b) What are the materials of construction of existing wells to be sampled? c) What were the methods of installation and development of existing wells to be sampled?

Also, the ground water plan discusses the installation and development of wells for obtaining hydrologic information and states that these wells may be used for chemical monitoring activities. If these wells could be used for either initial round sampling or detection monitoring at a later date, our policy is that the PVC casing described should not be allowed. Stainless steel or Teflon should be used.

RESPONSE:

The existing wells at the Ponce Municipal Landfill Facility are not included as part of the groundwater monitoring system for the site. Therefore, comments a, b, and c have not been addressed. Sections 1.1 and 4.1 of the Groundwater Monitoring Plan (Reference 8) have been amended to clarify that these wells will not be used as part of the groundwater monitoring system.

In a telephone conversation with Doug Pocze of the EPA on March 2, 1989, it was agreed that BFIP will install composite wells consisting of a stainless steel screen and a 10 foot section of well casing above the screen while the remaining well casing will consist of PVC. Stainless steel materials have been included in the description of the well materials in the Groundwater Monitoring Plan (Reference 8).

COMMENT:

3. The order of sample collection should be volatile organics, total organic halogens, total organic carbon, extractable organics, total metals, and cyanide.

RESPONSE:

A response is addressed in Revision 2 of the Groundwater Monitoring Plan (Reference 8).

COMMENT:

4. The equipment decontamination procedures detailed in Appendix D of the Cover Soil Sampling Work Plan and in equivalent appendices or sections of the other plans pertain to all sampling equipment (other than large), including ancillary equipment such as bowls and pans used to homogenize soil samples and any containers used

Also, the analytical parameters for initial ground water sampling detailed in the ground water plan differs from the parameters detailed in the QA plan.

To help clear up these matter, the QA plan should provide a table on RFA soil sampling and initial round water sampling activities which lists: a) the number of samples by matrix (e.g., soil, ground water, surface water), b) the number (or frequency) and type of field quality control samples (e.g., duplicates, trip, equipment rinsate), c) analytical parameters by sample matrix. All information provided in the associated sampling plans should be consistent with the table.

RESPONSE:

The original version (Revision 0) of the QA Plan was prepared to be read in conjunction with Revision 1 of the groundwater monitoring and soil sampling plans, which were being prepared at the time the QA Plan was submitted. Our letter transmitting the QA Plan to EPA explained this. Some of the inconsistencies cited by the reviewers appear to have arisen because the reviewers unknowingly compared the QA Plan to previous submittals of the other documents. Other inconsistencies may also have arisen because of last minute changes in Revision 1 of the groundwater monitoring and soil sampling plans that were not anticipated when the QA Plan was submitted. With this reponse we have attempted to clarify all the inconsistencies created by the timing of previous submittals.

Tables 3, 4, and 5 provide the information of numbers of samples, field quality control samples and analytical parameters for the soil, groundwater and surface water sampling, respectively. Several of the numbers provided are indicated as provisional as the number of samples, in some cases, will depend upon the conditions encountered in the field.

The text has been revised (see page 1) to clarify that the groundwater monitoring program for the site, as described in the Groundwater Monitoring Plan (Reference 8), includes both groundwater sampling and surface water sampling. Thus, the Groundwater Monitoring Plan sampling protocol, referenced in the QA Plan is for groundwater sampling and surface water sampling.

COMMENT:

2. Much more definitive information is needed regarding other aspects of RFA ground water sampling activities. a) How will samples be taken (i.e., bailer, bladder pump, etc.) from existing wells and what standard

Golder Associates Inc.
CONSULTING ENGINEERS

April 21, 1989 883-3643

BFI of Ponce, Inc.
757 North Eldridge
Houston, Texas 77079

Attn: Mr. Bruce Jernigan

RE: QUALITY ASSURANCE PLAN FOR LABORATORY ANALYSIS
AND FIELD INSTRUMENT MAINTENANCE
PONCE MUNICIPAL LANDFILL
PONCE, PUERTO RICO

Gentlemen:

Please find enclosed Revision 1 of the Quality Assurance Plan for Laboratory Analysis and Field Instrument Maintenance. This current version incorporates comments from the U.S. Environmental Protection Agency, Region II (EPA) regarding the October 19, 1988 submittal of the plan, as conveyed in the transmittals received on December 16, 1988 and January 4, 1989 from EPA. Their comments are listed below along with an response. The comments from the December 16, 1988 transmittal are numbered in the same sequence as they appear in the transmittal. Only one comment from the January 4, 1988 transmittal pertains to the quality assurance plan and is addressed as comment number 12, below.

COMMENT:

1. The quality assurance plan references the various sampling plans for information on RFA soil and first round ground water sampling activities. The documents on surface soil and subsurface soil provide clear information regarding at least the number of soil samples to be taken and analytical parameters. However, neither the ground water monitoring plan referenced by the QA plan nor the QA plan provides necessary information on initial water sampling activities. These two plans also are inconsistent.

   The ground water plan does not mention that six ground water samples will be taken as stated in the QA plan. The ground water plan and conversation with project personnel indicate that surface water samples may be taken also and they are not covered in the QA plan.

8.0 ANALYSIS AND DATA MANAGEMENT PLAN

8.1 Quality Assurance/Quality Control Procedures

These procedures are in the report entitled "Quality Assurance Plan for Laboratory Analysis and Field Instrument Maintenance, Ponce Municipal Landfill, Ponce, Puerto Rico" (Golder Associates Inc., 1988c).

8.2 Laboratory Contacts

The two laboratories proposed for this work are:

Environmental Sciences and Engineers, Inc. (ESE),
Gainesville, Florida
Jeff Shamis (904) 332-3318

Radian Corporation
Research Triangle Park, North Carolina
Cindy Spitter (919) 541-9100

8.3 Data Management

Results will be stored on a relational data base for review and reporting. All raw analytical data will be held by Golder Associates Inc. or the laboratory. Data will be presented to EPA in tabular and/or graphic forms.

7.5.2 Sample Holding and Shipment

Subsequent to sampling, the sample containers will be stored in an ice-packed container or shuttle. The sample shuttles will be transported so they are received at the laboratory within thirty-six hours after sample collection. The time between initial sample collection and laboratory analyses shall be kept to the minimum amount that is practical. The safest and most expedient methods of sample transport will be used.

Strict chain-of-custody procedures will be adhered to for all samples. From the time the sample is collected until the issuing of the analytical laboratory results, the samples will be in the custody of assigned personnel. In order to maintain custody, the samples will either be:

a) In sight of the assigned custodian,
b) Locked in a tamper-proof location, or
c) Sealed with a tamper-proof seal.

A written record of the transfer of samples will be maintained.

The Chain-of-Custody Record will be attached to the sample container at the time the sample is collected. All sample bottles will be correctly labeled. When transferring the possession of samples, the transferee should sign and record the date and time on the record. The number of custodians in the chain of possession will be as few as possible.

The Chain-of-Custody Record will be sealed in the sample shuttle and transported to the laboratory. Upon receipt by the lab, the seal will be broken, and the condition of the samples, date, and time will be recorded on the form by the person receiving the sample.

7.5 Sample Documentation and Shipment

7.5.1 Field Sampling and Chain-of-Custody

A chain-of-custody and sample parameter form will be appropriately completed for each sampling point. The following information will be documented on field sampling forms (Figure C-5) or in a GAI field log book:

a) Facility site code, sample code, sample point ID and other identifiers;

b) Date, clock time, and time elapsed (if greater than one hour) from start to finish of sampling;

c) Presence/absence of immiscible layers;

d) Depth to groundwater from the top of well pipe along with the time measured; (disregard for surface sample);

e) Information regarding purging of the well prior to sampling (disregard for surface sample);

f) Field test results including pH, temperature, specific conductance, and turbidity measurements;

g) Sampling method used, such as bailer, bladder pump, etc. (equipment material will be noted);

h) Type of sample, well sampling sequence, sample container type, preservatives used, parameters requested and other pertinent information (i.e. sampled in conjunction with regulatory authorities);

i) Field observations and sampling conditions (i.e. weather conditions);

j) Appearance of sample, such as color, turbidity, sediment, etc.; and

k) Internal temperature of field and shipping containers;

l) Name of transporter and name of laboratory to perform the analysis; and

m) Samplers' identification and signature.

~~allow collection with the sample container, the water will be collected with a new I-Chem 300 series container and carefully transferred to the sample container. The applicable sampling requirements and preservative procedures, as described in Section 7.2, will also be used for surface water sampling. The estimated number of surface water samples, duplicate samples, matrix spike samples, matrix spike duplicate samples, field blanks and trip blanks to be taken, for the various monitoring stages, are summarized in Table 7.~~

7.4 Field Parameter Measurements

Field parameter measurements will be taken for the groundwater and surface water samples obtained during sampling events, and for groundwater obtained during well development and during drilling. In each situation, the water samples will be collected in a clean, quart size, glass jar. This jar will be rinsed with the sample water, except for samples from low yield wells, and then filled in a manner which minimizes aeration of the sample. The measurement of temperature, pH, specific conductance, and turbidity of the sample will be taken using the appropriate meters and recorded on a field sampling documentation form (Figure C-5).

All meters used for the field measurements of pH, specific conductance, and turbidity will be calibrated prior to initial sampling. The calibration of field meters shall be checked daily before the start of sampling and every four hours and appropriately recalibrated during the sampling period. The meters and sample jars will be rinsed three times with distilled water before measurements are taken on another sample.

3. rinse with 10% HNO_3,

4. triple deionized water rinse, and

5. air dry.

l. At least one trip blank will be used for each sampling event at the site. If the water samples are obtained with dedicated pumps or bailers, no equipment will require decontamination and so no rinsate blanks will be used. If non-dedicated bailers are used a rinsate blank will be obtained from each batch of decontaminated bailers (see Appendix B). New polypropylene rope will be used at each hole and, therefore, no rinsate blank of the rope will be required. The estimated number of groundwater samples, duplicate samples, matrix spike samples, matrix spike duplicate samples, rinsate blanks, field blanks and trip blanks to be taken, for the various monitoring stages, are summarized in Table 6.

m. Sample containers will be sealed tight and placed in an ice-packed container or shuttle. The well cap will be replaced and the protective casing locked.

n. Sampling will be delayed if inclement weather conditions, such as heavy rain occurs. Such conditions may jeopardize the integrity of the samples and field measurements.

~~7.3 Surface Water Sampling~~

~~A surface water sampling station will be established within the gully in the eastern portion of the site. A concrete marker will be established on the bank of the gully to identify the sampling location.~~

~~The surface water sampling procedure will consist of taking the water sample at mid depth in the center of the flow path. Samples will be collected by merely submerging the laboratory sample container to the desired sampling depth; however, containers with preservatives cannot be lowered into the water. In a situation where a preservative is present in the sample container or if the water depth is too shallow to~~

test to be performed and the preservative which has been provided by the laboratory. Sample preservation, sample holding time, and sample containers to be used are summarized in Table 5. Sample containers should be number coded to match the Chain-of-Custody form.

g. The sampling of various parameters will be conducted in the following order:

1. Temperature, pH, specific conductance, and turbidity.

2. Volatile organic compounds.

3. PCB's and semivolatile organics.

4. Inorganic parameters.

5. Cyanide.

6. pH, and specific conductance.

h. Field parameters consisting of pH, specific conductance, turbidity and temperature will be obtained in triplicates for each groundwater monitoring sample at the initiation of the sampling event. If the turbidity reading is significantly above the baseline value established during well development (see Section 5.5) then the well in question will be redeveloped.

i. When sampling volatile organics with a bladder pump, the pump rate should be regulated so as to provide a slow continuous discharge rate of less than 100 ml/minute.

j. Sample vials for volatile organics should be filled so that no head space remains.

k. Filtration of appropriate samples will be performed within two hours of sample collection. Filtration will be done through a 0.45 micron cellulose ester filter and will be performed in the field. The filter device will be cleaned or decontaminated between filtering events. The decontamination procedure for the filter and other appropriate sampling equipment is:

1. wash and scrub with alconox detergent,

2. tap water rinse,

data exceeds 1000 ppm, or if visual inspection of the groundwater sample indicates the presence of a phase liquid. Lower an interface probe through the eductor pipe within the well and record the depths at which the probe indicates contrast as it moves through the liquid in the well. Retrieve the interface probe and rinse with the reel and probe with deionized water and isopropanol alcohol.

If an immiscible liquid is detected:

1. Calculate the thickness of the phase immiscible liquid.

2. Lower a bottom loading Teflon or stainless steel bailer through the eductor pipe until the bottom of the bailer is just above the immiscible/water interface or until the bailer is totally immersed in the immiscible liquid, whichever comes first. Retrieve the bailer and place the liquid in a sample container for laboratory analysis. A new polypropylene rope will be used to lower the bailer and will be discarded after its use.

d. Purge a minimum of three (3) times the volume of standing water in the well. Wells screened in low yielding formations may be purged to dryness if well recharge is insufficient to allow evacuation of 3 well volumes within a reasonable time (e.g. 3 days). Purging shall be performed using dedicated bladder pumps or bailers. A gas supply (compressed air or pure grade nitrogen) will be connected to the well assembly and released to the bladder pump via a control unit. At the end of the discharge cycle, the gas pressure is vented. Five to twenty pumping cycles are typically required to purge the air from the pump and outlet tubing.

e. The wells should be sampled immediately after purging. An evaluation of the recharge rate for the wells will be made using the recovery data obtained following well development. The lag time necessary for the well water to recovery before a water sample can be taken from the well will be determined from this data. This time frame will be included in a revised groundwater monitoring plan. A sample container will not be composited of groundwater from two different sampling periods.

f. All samples shall be placed in the appropriate prepared and laboratory cleaned containers. Each sample container should be labeled with the type of

Subsequent to well development and before the bladder pumps are installed in the wells, the presence of immiscible liquids in the groundwater will be evaluated. An interface probe will be lowered in the well slowly and the depths at which the probe indicates contrast as it moves through the liquid in the well will be recorded. If any immiscible layer is indicated, the thickness of the layer will be calculated.

7.2 Well Purging, Sampling, and Preservation Procedures

Subsequent to well development the test monitoring wells will be purged and sampled for the purpose of analytical testing. The procedures for sampling the test monitoring wells are listed below:

a. Sample the air in the well head for organic vapor immediately after removing the well cap. A photoionization detector will be used for this purpose. The results will be recorded.

b. Measure the depth of the static water surface to the nearest 0.01 feet in all the wells prior to well purging. Water level measurements will be taken using an electrical water level indicator. The following procedure will be used to measure and decontaminate an indicator when it is used to measure the depth to water in a monitoring well:

   1. Rinse the indicator probe off with deionized water, rinse the probe with a laboratory detergent solution (i.e. Alconox and deionized water), and again rinse the probe with deionized water. Shake off excess water and unreel the probe slowly down the eductor pipe until the light and buzzer of the indicator respond.

   2. After measuring the depth to static water, the cable is reeled back on the spool and the end is decontaminated again, following the procedure described above.

c. Check for an immiscible layer if non-aqueous phase liquids (NAPLs) have previously been detected, if any constituent has previously been detected at above 25% of its solubility, if the organic vapor

7.0 ~~PROPOSED~~ SAMPLING PROCEDURES

7.1 Well Sampling

Dedicated bladder pumps are currently proposed to be installed in each monitoring well for groundwater sampling purposes. However, evaluation of site hydrologic conditions upon completion of well installation may dictate alternative sampling methods.

A bladder or diaphragm pump is a type of pump which operates under the cycling of compressed gas. The compressed gas cycling inflates and deflates a diaphragm which creates a pumping action. The bladder pump will be made of stainless steel and Teflon material. Due to deep hole conditions, the pump may be supported by a clean stainless steel cable connected to the well cap. The pump intake should be positioned in the lower portion of the screened interval. A fluorocarbon resin (i.e. Teflon) outlet tube should be connected to the pump and extended to the well cap. Bladder pumps approved for well sampling shall operate in a continuous manner so that they do not produce a pulsating action which may aerate the groundwater samples in the outlet pipe or upon discharge.

A three cm (one-inch) diameter PVC eductor pipe will be placed inside the well casing to extend from the well cap to about 3 m (10 feet) above the highest anticipated water level in the well. The eductor pipe, therefore, will not be in direct contact with the well water. This pipe will serve as a conduit through which a water level indicator probe may be freely lowered to the water table without being obstructed by the discharge line and air line extending from the bladder pump.

INTRODUCTION

In the following sections, a statistical decision tree is constructed for the analysis of ground-water monitoring data. The decision points depend on the distributional form of the observed data and the detection frequency of each constituent. Statistical methods for each case are described in detail. Application of the statistical decision tree is illustrated with a series of hypothetical examples that reflect the possible ground-water monitoring outcomes at the Hovic facility for the proposed set of indicator parameters. Based on these hypothetical examples, statistical power characteristics are computed so that the effect magnitude required to balance false positive and false negative rates for each method may be identified precisely.

STATISTICAL METHODS

1. Case 1: Compounds Detected in All Background Samples

1.1 Compute the 95% prediction limit as:

$$\bar{x} + \sqrt{1 + \frac{1}{n}}\, t_{[n-1,\alpha/k]}\, s \tag{1}$$

where

$$\bar{x} = \sum_{i=1}^{n} \frac{x_i}{n} \tag{2}$$

$$s = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1}} \tag{3}$$

k is the number of monitoring wells, α is the false positive rate (set to $\alpha = .05$), $t_{[n-1,\alpha/k]}$ is the one-sided $(1 - \alpha/k)100\%$ point of Student's t distribution on $n - 1$ degrees of freedom, and n is the number of background measurements. Tables 1-3 provide values of the factor $t_{[n-1,\alpha/k]}\sqrt{1 + \frac{1}{n}}$ for values of $n = 4$ to 100 and $k = 1$ to 100; therefore, the owner/operator is only required to compute the mean $\bar{x}$ and standard deviation s of the n background measurements.

2. Case 2: Compounds Detected in at Least 10% of All Background Samples

2.1 Compute the mean of the n background samples as:

$$\bar{x} = \left(1 - \frac{n_0}{n}\right) \bar{x}' \tag{4}$$

where $\bar{x}'$ is the average of the n_1 detected values, and n_0 is the number of samples in which the compound is not detected or is below the method detection limit. The standard deviation is:

$$s = \sqrt{\left(1 - \frac{n_1}{n}\right)s'^2 + \frac{n_1}{n}\left(1 - \frac{n_0 - 1}{n - 1}\right)s'^2} \qquad (5)$$

where s' is the standard deviation of the n_1 detected measurements. The normal prediction limit can then be computed using the equation in section 1.1. This method is due to Aitchison (*J. Amer. Statistical Association*, 50, 901-908, 1955).

3. Case 3: Compounds Detected in 5% to 10% of All Background Samples (VOCs)

3.1 For each USEPA method 624 volatile organic priority pollutant scan, sum the detected concentrations across the 27 compounds listed in Table 4, substituting the published method detection limits (see Table 4) for those compounds that are not detected. For example, if none of the compounds were detected, the sum for that scan would be 154 *ppb*.

3.2 Compute the 95% poisson prediction limit (Gibbons, *Ground Water*, 25, 5, 572-580, 1987) as:

$$\frac{y}{n} + \frac{t^2}{2n} + \frac{t}{n}\sqrt{y(1+n) + \frac{t^2}{4}} \qquad (6)$$

where y is the total *ppb* for all n background scans (*i.e.*, the sum of n individual scan totals), n is the number of background scans, t is the $(1 - .05/k)100\%$ point of Student's t distribution on $n-1$ degrees of freedom (see Tables 5-7), and k is the number of monitoring wells.

3.3 Subtract the sum of the MDLs (*i.e.*, 154 *ppb*) from the computed limit value. The result is a limit value expressed as the number of detected *ppb* that is allowable in any single VOC scan.

3.4 When computed in this way, the estimated limit value is for the entire method 624 scan; therefore, the sum of detected values in a new monitoring scan should be compared to the limit and not individual values.

3.5 If only a small subset of the volatile organic compounds are used, or other inorganic parameters are detected in the 5% to 10% range, the limit in 3.2, can be computed for each compound individually. In this case, y is the sum of detected values (or MDL) for that compound across the n background measurements.

4. Compounds Detected in Less Than 5% of All Background Samples

4.1 The 95% assurance limits (*i.e.*, false positive and false negative rates set to 5%) are computed using the method due to Clayton, Hines and Elkins (*Analytical Chemistry*, 59, 2506-2514, 1987), using variance estimates from USEPA's round robin study (*Federal Register* October 26, 1984, 49, 201). The assurance limit is:

$$\phi\sqrt{1 + \frac{1}{n}}s \qquad (7)$$

where γ is the noncentrality parameter of the one-sided noncentral t distribution with $n-1$ degrees of freedom, and s is the standard deviation of n analytical replicates.

4.2 For the case of 7 analytical replicates required by USEPA and false positive and false negative rates of 5%, the assurance limit is:

$$3.75\sqrt{1+\frac{1}{7}}s = 4s \tag{8}$$

4.3 Values of s for the method 624 volatile organic priority pollutant compounds can be found on page 147 in Table 5 of the previously cited *Federal Register*. The corresponding 95% assurance limits are provided in Table 4.

ILLUSTRATION

To illustrate the previously defined statistical monitoring program, consider the hypothetical data in Table 8. These data reflect a monitoring program in which 2 background wells were monitored quarterly for a period of two years, yielding 16 background observations (*i.e.*, $n = 16$). Furthermore, we assume that 4 monitoring wells are to be evaluated on the next round of sampling.

Inspection of Table 8 reveals that chromium had a detection frequency of 44%, lead 100%, benzene was never detected and toluene was detected once (*i.e.*, 6%).

The prediction limit for chromium, for which 7 out of 16 values were detected, is computed as:

$$\bar{x} = \left(1-\frac{9}{16}\right)38.57 = 16.87 \tag{9}$$

$$s = \sqrt{\left(1-\frac{9}{16}\right)17.73^2 + \frac{9}{16}\left(1-\frac{9-1}{16-1}\right)38.57^2} \tag{10}$$

$$limit = 16.87 + 2.57(22.98) = 75.93 ppb \tag{11}$$

where 2.57 is the multiplication factor for $n = 16$ and $k = 4$ from Table 1.

The prediction limit for lead, where all background measurements were detected, is computed as:

$$limit = 31.31 + 2.57(17.04) = 75.10 ppb \tag{12}$$

Since none of the benzene measurements were detected, we use the assurance limit of 27.6 *ppb* as the limit for this compound.

Finally, since the single detected value of toluene yielded a detection frequency of 6%, we can compute a poisson prediction limit for this compound. Substituting the detection limit of 6 *ppb* for the 15 nondetected measurements, we find that $y = 110 ppb$ and $t = 2.49$ (see Table 5); therefore,

$$limit = \frac{110}{16} + \frac{2.49^2}{2(16)} + \frac{2.49}{16}\sqrt{110(1+16)+\frac{2.49^2}{4}} = 13.8 ppb \tag{13}$$

which is in fact, less than the assurance limit of 19.2 *ppb* for this compound.

STATISTICAL POWER

Statistical power curves are presented in Figures 1-3 for chromium, lead and toluene. Inspection of Figure 1, which is based on the hypothetical data in Table 8, reveals that for 16 background samples, 4 future monitoring wells, and a background mean and standard deviation of 16.87 ± 22.98, the test reaches a balance of false positive and false negative rates of 5% (*i.e.*, 95% power) at a concentration of 100 $\mu g/l$ in any single new monitoring well. Figure 2 reveals that for lead, 95% power is achieved at a monitoring concentration of 93 $\mu g/l$. Figure 3 reveals that for toluene, the poisson prediction limit achieves 95% power at a concentration of 16 $\mu g/l$. These power calculations are based on 100 replications simulated from normal and poisson distributions respectively.

The assurance limit of 27.6 $\mu g/l$ for benzene insures both false positive and false negative rates of 5% (*i.e.*, power = .95) for the test of the null hypothesis that the concentration of benzene is zero.

LIMIT ESTIMATES FOR THE FIRST 2 YEARS OF MONITORING

In the absence of a sufficient historical database, assurance limits for chromium, lead, benzene and toluene will be used for the first two years of quarterly monitoring at the Hovic facility. Assurance limits for benzene and toluene are 27.6 *ppb* and 19.2 *ppb* respectively (see Table 4). For chromium, a standard deviation of 5.7 *ppb* was reported for a spiking concentration of 150 *ppb* (*Federal Register*, 49, 209, Friday October 26, 1984, page 204); therefore, the 95% assurance limit is 4(5.7)=22.8 *ppb*. For lead, a spiking concentration of 24 *ppb* yielded a standard deviation of 9.6 *ppb*; therefore, the assurance limit is 4(9.6)=38.4 *ppb*. Any new monitoring value exceeding these assurance limits will be considered a "trigger" value.

BACKGROUND SAMPLING DESIGN

Given that the proposed indicator parameters are expected to be rarely detected in the upgradient wells we propose that the background database be continuously updated with each new set of quarterly measurements. For those compounds that are never detected, this increased background database will not require any recomputation of the assurance limits that have already been proposed for the first two years of ground-water detection monitoring. For those compounds that are detected in 5% or more of the total number of background samples, limit values will be recomputed quarterly.

TABLE 1

FACTORS FOR OBTAINING ONE-SIDED 95% PREDICTION LIMITS FOR k ADDITIONAL SAMPLES GIVEN A BACKGROUND SAMPLE OF SIZE n

Previous n	Number of new measurements (k)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	2.63	3.56	4.18	4.67	5.06	5.43	5.74	6.03	6.29	6.53	6.76	6.97	7.17	7.36	7.54
5	2.34	3.04	3.49	3.83	4.10	4.34	4.54	4.73	4.89	5.04	5.18	5.31	5.44	5.55	5.66
6	2.18	2.78	3.14	3.42	3.63	3.82	3.97	4.11	4.24	4.35	4.46	4.56	4.65	4.73	4.81
7	2.08	2.62	2.94	3.17	3.36	3.51	3.65	3.76	3.87	3.96	4.05	4.13	4.20	4.27	4.34
8	2.01	2.51	2.80	3.01	3.18	3.32	3.43	3.54	3.63	3.71	3.79	3.86	3.92	3.98	4.04
9	1.96	2.43	2.70	2.90	3.06	3.18	3.29	3.38	3.46	3.54	3.60	3.67	3.72	3.78	3.83
10	1.92	2.37	2.63	2.82	2.96	3.08	3.18	3.26	3.34	3.41	3.47	3.53	3.58	3.63	3.68
11	1.89	2.33	2.58	2.75	2.89	3.00	3.09	3.17	3.25	3.31	3.37	3.42	3.47	3.52	3.56
12	1.87	2.29	2.53	2.70	2.83	2.93	3.02	3.10	3.17	3.23	3.29	3.34	3.39	3.43	3.47
13	1.85	2.26	2.49	2.66	2.78	2.88	2.97	3.04	3.11	3.17	3.23	3.27	3.32	3.36	3.40
14	1.83	2.24	2.46	2.62	2.74	2.84	2.93	3.00	3.06	3.13	3.17	3.22	3.26	3.30	3.34
15	1.82	2.21	2.44	2.59	2.71	2.81	2.89	2.96	3.02	3.07	3.12	3.17	3.21	3.25	3.28
16	1.81	2.20	2.41	2.57	2.68	2.78	2.85	2.92	2.98	3.04	3.09	3.13	3.17	3.21	3.24
17	1.80	2.18	2.40	2.54	2.66	2.75	2.83	2.89	2.96	3.01	3.05	3.09	3.13	3.17	3.21
18	1.79	2.17	2.38	2.53	2.64	2.73	2.80	2.87	2.93	2.98	3.02	3.07	3.10	3.14	3.17
19	1.78	2.16	2.36	2.51	2.62	2.71	2.78	2.85	2.90	2.95	3.00	3.04	3.08	3.11	3.14
20	1.77	2.14	2.35	2.49	2.60	2.69	2.76	2.83	2.88	2.93	2.98	3.02	3.05	3.09	3.12
21	1.77	2.13	2.34	2.48	2.59	2.67	2.75	2.81	2.86	2.91	2.96	3.00	3.03	3.07	3.10
22	1.76	2.13	2.33	2.47	2.57	2.66	2.73	2.79	2.85	2.89	2.94	2.98	3.01	3.05	3.08
23	1.75	2.12	2.32	2.46	2.56	2.65	2.72	2.78	2.83	2.88	2.92	2.96	3.00	3.03	3.06
24	1.75	2.11	2.31	2.45	2.55	2.63	2.70	2.76	2.82	2.87	2.91	2.95	2.98	3.01	3.04
25	1.74	2.10	2.30	2.44	2.54	2.62	2.69	2.75	2.81	2.85	2.89	2.93	2.97	3.00	3.03
26	1.74	2.10	2.29	2.43	2.53	2.61	2.68	2.74	2.79	2.84	2.88	2.92	2.96	2.99	3.01
27	1.74	2.09	2.29	2.42	2.52	2.61	2.67	2.73	2.78	2.83	2.87	2.91	2.94	2.97	3.00
28	1.73	2.09	2.28	2.42	2.52	2.60	2.66	2.72	2.77	2.82	2.86	2.90	2.93	2.96	2.99
29	1.73	2.08	2.28	2.41	2.51	2.59	2.66	2.71	2.77	2.81	2.85	2.89	2.92	2.95	2.98
30	1.73	2.08	2.27	2.40	2.50	2.58	2.65	2.71	2.76	2.80	2.84	2.88	2.91	2.94	2.97
31	1.73	2.07	2.27	2.40	2.50	2.58	2.64	2.70	2.75	2.79	2.83	2.87	2.90	2.93	2.96
32	1.72	2.07	2.26	2.39	2.49	2.57	2.64	2.69	2.74	2.79	2.83	2.86	2.89	2.92	2.95
33	1.72	2.07	2.26	2.39	2.49	2.56	2.63	2.69	2.74	2.78	2.82	2.85	2.89	2.92	2.94
34	1.72	2.06	2.25	2.38	2.48	2.56	2.62	2.68	2.73	2.77	2.81	2.85	2.88	2.91	2.94
35	1.71	2.06	2.25	2.38	2.48	2.55	2.62	2.67	2.72	2.77	2.81	2.84	2.87	2.90	2.93
36	1.71	2.06	2.25	2.37	2.47	2.55	2.61	2.67	2.72	2.76	2.80	2.83	2.87	2.90	2.92
37	1.71	2.06	2.24	2.37	2.47	2.54	2.61	2.66	2.71	2.76	2.79	2.83	2.86	2.89	2.92
38	1.71	2.06	2.24	2.37	2.46	2.54	2.60	2.66	2.71	2.75	2.79	2.82	2.86	2.88	2.91
39	1.71	2.05	2.24	2.36	2.46	2.54	2.60	2.66	2.70	2.75	2.78	2.82	2.85	2.88	2.91
40	1.71	2.05	2.23	2.36	2.46	2.53	2.60	2.65	2.70	2.74	2.78	2.81	2.85	2.87	2.90
41	1.70	2.05	2.23	2.36	2.45	2.53	2.59	2.65	2.69	2.74	2.77	2.81	2.84	2.87	2.90
42	1.70	2.04	2.23	2.35	2.45	2.53	2.59	2.64	2.69	2.73	2.77	2.80	2.84	2.87	2.89
43	1.70	2.04	2.23	2.35	2.45	2.52	2.59	2.64	2.69	2.73	2.77	2.80	2.83	2.86	2.89
44	1.70	2.04	2.22	2.35	2.44	2.52	2.58	2.64	2.68	2.73	2.76	2.80	2.83	2.86	2.88
45	1.70	2.04	2.22	2.35	2.44	2.52	2.58	2.63	2.68	2.72	2.76	2.79	2.82	2.85	2.88
46	1.70	2.04	2.22	2.34	2.44	2.51	2.58	2.63	2.68	2.72	2.76	2.79	2.82	2.85	2.88
47	1.70	2.03	2.22	2.34	2.44	2.51	2.57	2.63	2.67	2.72	2.75	2.79	2.82	2.85	2.87
48	1.70	2.03	2.22	2.34	2.43	2.51	2.57	2.62	2.67	2.71	2.75	2.78	2.81	2.84	2.87
49	1.69	2.03	2.21	2.34	2.43	2.51	2.57	2.62	2.67	2.71	2.75	2.78	2.81	2.84	2.87
50	1.69	2.03	2.21	2.34	2.43	2.50	2.57	2.62	2.67	2.71	2.74	2.78	2.81	2.84	2.86
60	1.68	2.02	2.20	2.32	2.41	2.48	2.55	2.60	2.64	2.68	2.72	2.75	2.78	2.81	2.84
70	1.68	2.01	2.19	2.31	2.40	2.47	2.53	2.58	2.63	2.67	2.70	2.74	2.77	2.79	2.82
80	1.67	2.00	2.18	2.30	2.39	2.46	2.52	2.57	2.62	2.66	2.69	2.73	2.75	2.78	2.80
90	1.67	2.00	2.17	2.29	2.38	2.45	2.51	2.56	2.61	2.65	2.68	2.71	2.74	2.77	2.79
100	1.67	1.99	2.17	2.29	2.38	2.45	2.51	2.56	2.60	2.64	2.67	2.71	2.73	2.76	2.79

Factor = $t_{(n-1,1-\alpha/k)}\sqrt{1 + 1/n}$

TABLE 3

FACTORS FOR OBTAINING ONE-SIDED 95% PREDICTION LIMITS FOR k ADDITIONAL SAMPLES GIVEN A BACKGROUND SAMPLE OF SIZE n

Previous n	Number of new measurements (k)														
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
4	7.71	7.87	8.03	8.19	8.33	8.48	8.61	8.75	8.88	9.00	9.13	9.26	9.38	9.48	9.59
5	5.76	5.86	5.95	6.06	6.13	6.21	6.29	6.37	6.45	6.52	6.59	6.66	6.72	6.79	6.85
6	4.89	4.96	5.03	5.09	5.15	5.22	5.27	5.33	5.38	5.43	5.48	5.53	5.58	5.62	5.67
7	4.40	4.46	4.51	4.56	4.61	4.66	4.71	4.75	4.80	4.84	4.88	4.91	4.96	4.99	5.02
8	4.09	4.14	4.19	4.23	4.27	4.31	4.35	4.39	4.43	4.46	4.50	4.53	4.56	4.59	4.62
9	3.87	3.92	3.96	4.00	4.04	4.08	4.11	4.14	4.18	4.21	4.24	4.26	4.29	4.32	4.34
10	3.72	3.76	3.80	3.83	3.87	3.90	3.93	3.96	3.99	4.02	4.05	4.07	4.10	4.13	4.15
11	3.60	3.64	3.67	3.71	3.74	3.77	3.80	3.83	3.86	3.88	3.91	3.93	3.96	3.98	4.00
12	3.51	3.54	3.58	3.61	3.64	3.67	3.70	3.73	3.75	3.77	3.79	3.82	3.84	3.86	3.88
13	3.43	3.47	3.50	3.53	3.56	3.58	3.61	3.64	3.66	3.68	3.71	3.73	3.75	3.77	3.79
14	3.37	3.40	3.43	3.46	3.49	3.52	3.54	3.57	3.59	3.61	3.63	3.65	3.67	3.69	3.71
15	3.32	3.35	3.38	3.41	3.43	3.46	3.48	3.51	3.53	3.55	3.57	3.59	3.61	3.63	3.64
16	3.27	3.30	3.33	3.36	3.39	3.41	3.43	3.46	3.48	3.50	3.52	3.54	3.56	3.57	3.59
17	3.24	3.27	3.29	3.32	3.35	3.37	3.39	3.41	3.44	3.46	3.47	3.49	3.51	3.53	3.54
18	3.20	3.23	3.26	3.29	3.31	3.33	3.36	3.38	3.40	3.42	3.44	3.45	3.47	3.49	3.50
19	3.18	3.20	3.23	3.26	3.28	3.30	3.32	3.34	3.36	3.38	3.40	3.42	3.44	3.45	3.47
20	3.15	3.18	3.20	3.23	3.25	3.27	3.30	3.32	3.33	3.35	3.37	3.39	3.40	3.42	3.44
21	3.13	3.15	3.18	3.20	3.23	3.25	3.27	3.29	3.31	3.33	3.34	3.36	3.38	3.39	3.41
22	3.11	3.13	3.16	3.18	3.21	3.23	3.25	3.27	3.29	3.30	3.32	3.34	3.35	3.37	3.38
23	3.09	3.11	3.14	3.16	3.19	3.21	3.23	3.25	3.26	3.28	3.30	3.32	3.33	3.35	3.36
24	3.07	3.10	3.12	3.15	3.17	3.19	3.21	3.23	3.25	3.26	3.28	3.30	3.31	3.33	3.34
25	3.06	3.08	3.11	3.13	3.15	3.17	3.19	3.21	3.23	3.25	3.26	3.28	3.29	3.31	3.32
26	3.04	3.07	3.09	3.11	3.14	3.16	3.18	3.19	3.21	3.23	3.25	3.26	3.28	3.29	3.31
27	3.03	3.06	3.08	3.10	3.12	3.14	3.16	3.18	3.20	3.22	3.23	3.25	3.26	3.28	3.29
28	3.02	3.04	3.07	3.09	3.11	3.13	3.15	3.17	3.19	3.20	3.22	3.23	3.25	3.26	3.28
29	3.01	3.03	3.06	3.08	3.10	3.12	3.14	3.16	3.17	3.19	3.20	3.22	3.23	3.25	3.26
30	3.00	3.02	3.04	3.07	3.09	3.11	3.13	3.14	3.16	3.18	3.19	3.21	3.22	3.24	3.25
31	2.99	3.01	3.04	3.06	3.08	3.10	3.12	3.13	3.15	3.17	3.18	3.20	3.21	3.23	3.24
32	2.98	3.00	3.03	3.06	3.07	3.09	3.11	3.12	3.14	3.16	3.17	3.19	3.20	3.22	3.23
33	2.97	2.99	3.02	3.04	3.06	3.08	3.10	3.11	3.13	3.15	3.16	3.18	3.19	3.21	3.22
34	2.96	2.99	3.01	3.03	3.05	3.07	3.09	3.11	3.12	3.14	3.15	3.17	3.18	3.20	3.21
35	2.96	2.98	3.00	3.02	3.04	3.06	3.08	3.10	3.12	3.13	3.15	3.16	3.17	3.19	3.20
36	2.95	2.97	3.00	3.02	3.04	3.06	3.07	3.09	3.11	3.13	3.14	3.16	3.17	3.18	3.19
37	2.94	2.97	2.99	3.01	3.03	3.05	3.07	3.08	3.10	3.12	3.13	3.15	3.16	3.17	3.19
38	2.94	2.96	2.98	3.00	3.02	3.04	3.06	3.08	3.09	3.11	3.12	3.14	3.15	3.17	3.18
39	2.93	2.96	2.98	3.00	3.02	3.04	3.06	3.07	3.09	3.10	3.12	3.13	3.15	3.16	3.17
40	2.93	2.96	2.97	2.99	3.01	3.03	3.05	3.07	3.08	3.10	3.11	3.13	3.14	3.15	3.17
41	2.92	2.94	2.97	2.99	3.01	3.03	3.04	3.06	3.08	3.09	3.11	3.12	3.13	3.15	3.16
42	2.92	2.94	2.96	2.98	3.00	3.02	3.04	3.06	3.07	3.09	3.10	3.12	3.13	3.14	3.15
43	2.91	2.94	2.96	2.98	3.00	3.02	3.03	3.05	3.07	3.08	3.10	3.11	3.12	3.13	3.15
44	2.91	2.93	2.95	2.97	2.99	3.01	3.03	3.04	3.06	3.08	3.09	3.11	3.12	3.13	3.14
45	2.90	2.93	2.95	2.97	2.99	3.01	3.02	3.04	3.06	3.07	3.09	3.10	3.11	3.13	3.14
46	2.90	2.92	2.94	2.96	2.98	3.00	3.02	3.04	3.05	3.07	3.08	3.10	3.11	3.12	3.13
47	2.90	2.92	2.94	2.96	2.98	3.00	3.02	3.03	3.05	3.07	3.08	3.09	3.11	3.12	3.13
48	2.89	2.92	2.94	2.96	2.98	2.99	3.01	3.03	3.04	3.06	3.07	3.09	3.10	3.12	3.13
49	2.89	2.91	2.93	2.96	2.97	2.99	3.01	3.02	3.04	3.05	3.07	3.09	3.10	3.11	3.12
50	2.89	2.91	2.93	2.95	2.97	2.99	3.00	3.02	3.04	3.06	3.07	3.08	3.10	3.11	3.12
60	2.86	2.88	2.90	2.92	2.94	2.96	2.97	2.99	3.01	3.02	3.03	3.05	3.06	3.07	3.08
70	2.84	2.86	2.88	2.90	2.92	2.94	2.95	2.97	2.98	3.00	3.01	3.03	3.04	3.05	3.06
80	2.83	2.85	2.87	2.89	2.91	2.92	2.94	2.96	2.97	2.98	3.00	3.01	3.02	3.03	3.05
90	2.82	2.84	2.86	2.88	2.89	2.91	2.93	2.94	2.96	2.97	2.98	3.00	3.01	3.02	3.03
100	2.81	2.83	2.85	2.87	2.89	2.90	2.92	2.93	2.95	2.96	2.98	2.99	3.00	3.01	3.02

Factor = $t_{(\alpha=1.1-\alpha/k)}\sqrt{1 + 1/n}$

TABLE 3

FACTORS FOR OBTAINING ONE-SIDED 95% PREDICTION LIMITS FOR k ADDITIONAL SAMPLES GIVEN A BACKGROUND SAMPLE OF SIZE n

Previous n	Number of new measurements (k)													
	30	35	40	45	50	55	60	65	70	75	80	85	90	95
4	9.59	10.11	10.58	11.02	11.42	11.80	12.15	12.49	12.80	13.11	13.40	13.68	13.94	14.20
5	6.85	7.14	7.40	7.64	7.86	8.06	8.25	8.42	8.59	8.75	8.90	9.04	9.18	9.31
6	5.67	5.87	6.05	6.22	6.37	6.50	6.63	6.75	6.86	6.97	7.08	7.16	7.25	7.34
7	5.02	5.18	5.32	5.45	5.57	5.67	5.77	5.86	5.96	6.05	6.10	6.17	6.24	6.31
8	4.62	4.75	4.87	4.98	5.07	5.16	5.24	5.32	5.39	5.46	5.52	5.58	5.63	5.68
9	4.34	4.46	4.57	4.66	4.74	4.82	4.89	4.96	5.02	5.07	5.13	5.18	5.23	5.27
10	4.15	4.25	4.35	4.43	4.51	4.57	4.64	4.69	4.75	4.80	4.85	4.89	4.93	4.98
11	4.00	4.10	4.18	4.26	4.33	4.39	4.45	4.50	4.55	4.60	4.64	4.68	4.72	4.76
12	3.88	3.97	4.06	4.13	4.19	4.25	4.30	4.36	4.40	4.44	4.48	4.52	4.55	4.59
13	3.79	3.87	3.95	4.02	4.08	4.13	4.18	4.23	4.27	4.31	4.35	4.39	4.42	4.45
14	3.71	3.79	3.86	3.93	3.99	4.04	4.09	4.13	4.17	4.21	4.25	4.28	4.31	4.34
15	3.64	3.72	3.79	3.86	3.91	3.96	4.01	4.05	4.09	4.12	4.16	4.19	4.22	4.25
16	3.59	3.67	3.74	3.79	3.85	3.90	3.94	3.98	4.02	4.06	4.08	4.11	4.14	4.17
17	3.54	3.62	3.68	3.74	3.79	3.84	3.88	3.92	3.96	3.99	4.02	4.05	4.08	4.11
18	3.50	3.58	3.64	3.70	3.75	3.79	3.83	3.87	3.90	3.94	3.97	4.00	4.02	4.05
19	3.47	3.54	3.60	3.66	3.70	3.75	3.79	3.82	3.86	3.89	3.92	3.95	3.97	4.00
20	3.44	3.51	3.57	3.62	3.67	3.71	3.75	3.79	3.82	3.85	3.88	3.91	3.93	3.96
21	3.41	3.48	3.54	3.59	3.63	3.68	3.72	3.75	3.78	3.81	3.84	3.87	3.89	3.92
22	3.38	3.45	3.51	3.56	3.61	3.65	3.68	3.72	3.75	3.78	3.81	3.84	3.86	3.88
23	3.36	3.43	3.49	3.54	3.58	3.62	3.66	3.69	3.73	3.75	3.78	3.81	3.83	3.86
24	3.34	3.41	3.46	3.51	3.56	3.60	3.63	3.67	3.70	3.73	3.75	3.78	3.80	3.83
25	3.32	3.39	3.44	3.49	3.53	3.57	3.61	3.64	3.67	3.70	3.73	3.75	3.78	3.80
26	3.31	3.37	3.42	3.47	3.52	3.55	3.59	3.62	3.65	3.68	3.71	3.73	3.75	3.78
27	3.29	3.35	3.41	3.46	3.50	3.54	3.57	3.60	3.63	3.66	3.69	3.71	3.73	3.75
28	3.28	3.34	3.39	3.44	3.48	3.52	3.55	3.59	3.61	3.64	3.67	3.69	3.71	3.73
29	3.26	3.32	3.38	3.42	3.47	3.50	3.54	3.57	3.60	3.62	3.65	3.67	3.70	3.72
30	3.25	3.31	3.36	3.41	3.45	3.49	3.52	3.55	3.58	3.61	3.63	3.66	3.68	3.70
31	3.24	3.30	3.35	3.40	3.44	3.48	3.51	3.54	3.57	3.59	3.62	3.64	3.66	3.68
32	3.23	3.29	3.34	3.39	3.43	3.46	3.50	3.53	3.55	3.58	3.61	3.63	3.65	3.67
33	3.22	3.28	3.33	3.38	3.42	3.45	3.48	3.51	3.54	3.57	3.59	3.62	3.64	3.66
34	3.21	3.27	3.32	3.37	3.41	3.44	3.47	3.50	3.53	3.56	3.58	3.60	3.62	3.64
35	3.20	3.26	3.31	3.35	3.39	3.43	3.46	3.49	3.52	3.55	3.57	3.59	3.61	3.63
36	3.19	3.25	3.30	3.35	3.39	3.42	3.45	3.48	3.51	3.54	3.56	3.58	3.60	3.62
37	3.19	3.24	3.29	3.34	3.38	3.41	3.44	3.47	3.50	3.53	3.55	3.57	3.59	3.61
38	3.18	3.24	3.29	3.33	3.37	3.40	3.44	3.46	3.49	3.52	3.54	3.56	3.58	3.60
39	3.17	3.23	3.28	3.32	3.36	3.40	3.43	3.46	3.48	3.51	3.53	3.55	3.57	3.59
40	3.17	3.22	3.27	3.31	3.35	3.39	3.43	3.45	3.47	3.50	3.52	3.54	3.56	3.58
41	3.16	3.22	3.27	3.31	3.35	3.38	3.41	3.44	3.47	3.49	3.51	3.54	3.56	3.58
42	3.15	3.21	3.26	3.30	3.34	3.37	3.41	3.43	3.46	3.48	3.51	3.53	3.55	3.57
43	3.15	3.20	3.25	3.30	3.33	3.37	3.40	3.43	3.45	3.48	3.50	3.52	3.54	3.56
44	3.14	3.20	3.25	3.29	3.33	3.36	3.39	3.42	3.45	3.47	3.49	3.51	3.53	3.55
45	3.14	3.19	3.24	3.28	3.32	3.36	3.39	3.41	3.44	3.46	3.49	3.51	3.53	3.55
46	3.13	3.19	3.24	3.28	3.32	3.35	3.38	3.41	3.43	3.46	3.48	3.50	3.52	3.54
47	3.13	3.18	3.23	3.27	3.31	3.34	3.38	3.40	3.43	3.45	3.48	3.50	3.52	3.53
48	3.12	3.18	3.23	3.27	3.31	3.34	3.37	3.40	3.42	3.45	3.47	3.49	3.51	3.53
49	3.12	3.18	3.22	3.26	3.30	3.34	3.37	3.39	3.42	3.44	3.46	3.48	3.50	3.52
50	3.12	3.17	3.22	3.26	3.30	3.33	3.36	3.39	3.41	3.44	3.46	3.48	3.50	3.52
60	3.08	3.14	3.18	3.22	3.26	3.29	3.32	3.35	3.37	3.40	3.42	3.44	3.46	3.47
70	3.06	3.12	3.16	3.20	3.24	3.27	3.30	3.33	3.35	3.37	3.39	3.41	3.43	3.45
80	3.05	3.10	3.14	3.18	3.22	3.25	3.28	3.30	3.33	3.35	3.37	3.39	3.41	3.42
90	3.03	3.08	3.13	3.17	3.20	3.23	3.26	3.29	3.31	3.33	3.35	3.37	3.39	3.41
100	3.02	3.07	3.12	3.16	3.19	3.22	3.25	3.27	3.30	3.32	3.34	3.36	3.38	3.39

Factor = $t_{(n-1,1-\alpha/k)}\sqrt{1 + 1/n}$

TABLE 4

Method 624 Volatile Organic Compounds
Published Method Detection Limits and
95% Assurance Limits in *ppb*

Compound	Reported MDL	Round-Robin SD	Assurance Limit
Benzene	4.4	6.9	27.6
Bromodichloromethane	2.2	6.4	25.6
Bromoform	4.7	5.4	21.6
Bromomethane	10.0	17.9	71.6
Carbon Tetrachloride	2.8	5.2	20.8
Chlorobenzene	6.0	6.3	25.2
Chloroethane	10.0	11.4	45.6
Chloroform	1.6	6.1	24.4
Chloromethane	10.0	19.8	79.2
Dibromochloromethane	3.1	6.1	24.4
1,1-Dichloroethane	4.7	5.1	20.4
1,2-Dichloroethane	2.8	6.0	24.0
1,1-Dichloroethene	2.8	9.1	36.4
trans-1,2-Dichloroethene	10.0	5.7	22.8
1,2-Dichloropropane	6.0	13.8	55.2
cis-1,3-Dichloropropene	5.0	15.8	63.2
trans-1,3-Dichloropropene	10.0	10.4	41.6
Ethyl Benzene	7.2	7.5	30.0
Methylene Chloride	2.8	7.4	29.6
1,1,2,2-Tetrachloroethane	6.9	7.4	29.6
Tetrachloroethene	4.1	5.0	20.0
Toluene	6.0	4.8	19.2
1,1,1-Trichloroethane	3.8	4.6	18.4
1,1,2-Trichloroethane	5.0	5.5	22.0
Trichloroethene	1.9	6.6	26.4
Trichlorofluoromethane	10.0	10.0	40.0
Vinyl Chloride	10.0	20.0	80.0

all values reported in $\mu g/l$

Assurance Limit = $3.75\sqrt{1 + 1/7}SD = 4.0(SD)$

where 3.75 is the noncentrality parameter of the one-sided noncentral t distribution with 6 degrees of freedom, that is, 7 replicates and $\alpha = \beta = .05$

TABLE 5

VALUES OF t FOR OBTAINING ONE-SIDED 95% POISSON PREDICTION LIMITS FOR k ADDITIONAL SAMPLES GIVEN A BACKGROUND SAMPLE OF SIZE n

Previous n	Number of new measurements (k)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	2.36	3.18	3.74	4.18	4.54	4.86	5.14	5.39	5.62	5.84	6.04	6.23	6.41	6.58	6.74
5	2.13	2.78	3.19	3.50	3.76	3.98	4.18	4.31	4.47	4.60	4.73	4.85	4.96	5.07	5.17
6	2.01	2.57	2.91	3.16	3.36	3.53	3.68	3.81	3.93	4.03	4.13	4.22	4.30	4.38	4.45
7	1.94	2.45	2.75	2.97	3.14	3.29	3.41	3.52	3.62	3.71	3.79	3.86	3.93	4.00	4.06
8	1.89	2.36	2.64	2.84	3.00	3.13	3.24	3.33	3.42	3.50	3.57	3.64	3.70	3.75	3.81
9	1.86	2.31	2.57	2.75	2.90	3.02	3.12	3.21	3.28	3.35	3.42	3.48	3.53	3.58	3.63
10	1.83	2.26	2.51	2.68	2.82	2.93	3.03	3.11	3.18	3.25	3.31	3.36	3.41	3.46	3.50
11	1.81	2.23	2.47	2.63	2.76	2.87	2.96	3.04	3.11	3.17	3.22	3.28	3.32	3.37	3.41
12	1.80	2.20	2.43	2.59	2.72	2.82	2.91	2.98	3.06	3.11	3.16	3.21	3.25	3.29	3.33
13	1.78	2.18	2.40	2.56	2.68	2.78	2.86	2.93	3.00	3.06	3.11	3.15	3.20	3.23	3.27
14	1.77	2.16	2.38	2.53	2.65	2.75	2.83	2.90	2.96	3.01	3.06	3.11	3.15	3.19	3.22
15	1.76	2.14	2.36	2.51	2.62	2.72	2.80	2.86	2.92	2.98	3.02	3.07	3.11	3.15	3.18
16	1.75	2.13	2.34	2.49	2.60	2.69	2.77	2.84	2.89	2.95	2.99	3.04	3.07	3.11	3.15
17	1.75	2.12	2.33	2.47	2.58	2.67	2.75	2.81	2.87	2.92	2.97	3.01	3.06	3.08	3.11
18	1.74	2.11	2.31	2.46	2.57	2.65	2.73	2.79	2.85	2.90	2.94	2.98	3.02	3.06	3.09
19	1.73	2.10	2.30	2.44	2.55	2.64	2.71	2.77	2.83	2.88	2.92	2.96	3.00	3.03	3.07
20	1.73	2.09	2.29	2.43	2.54	2.62	2.70	2.76	2.81	2.86	2.90	2.94	2.98	3.01	3.04
21	1.72	2.09	2.28	2.42	2.53	2.61	2.68	2.74	2.80	2.84	2.89	2.93	2.96	3.00	3.03
22	1.72	2.08	2.28	2.41	2.52	2.60	2.67	2.73	2.78	2.83	2.87	2.91	2.95	2.98	3.01
23	1.72	2.07	2.27	2.40	2.51	2.59	2.66	2.72	2.77	2.82	2.86	2.90	2.93	2.96	2.99
24	1.71	2.07	2.26	2.40	2.50	2.58	2.65	2.71	2.76	2.81	2.85	2.89	2.92	2.95	2.98
25	1.71	2.06	2.26	2.39	2.49	2.57	2.64	2.70	2.75	2.80	2.84	2.88	2.91	2.94	2.97
26	1.71	2.06	2.25	2.38	2.48	2.57	2.63	2.69	2.74	2.79	2.83	2.86	2.90	2.93	2.96
27	1.71	2.06	2.25	2.38	2.48	2.56	2.63	2.68	2.73	2.78	2.82	2.85	2.89	2.92	2.96
28	1.70	2.06	2.24	2.37	2.47	2.55	2.62	2.68	2.73	2.77	2.81	2.85	2.88	2.91	2.94
29	1.70	2.06	2.24	2.37	2.47	2.55	2.61	2.67	2.72	2.76	2.80	2.84	2.87	2.90	2.93
30	1.70	2.05	2.23	2.36	2.46	2.54	2.61	2.66	2.71	2.76	2.80	2.83	2.86	2.89	2.92
31	1.70	2.04	2.23	2.36	2.46	2.54	2.60	2.66	2.71	2.75	2.79	2.82	2.86	2.89	2.91
32	1.70	2.04	2.23	2.36	2.45	2.53	2.60	2.65	2.70	2.74	2.78	2.82	2.85	2.88	2.91
33	1.69	2.04	2.22	2.35	2.45	2.53	2.59	2.65	2.70	2.74	2.78	2.81	2.84	2.87	2.90
34	1.69	2.03	2.22	2.35	2.44	2.52	2.59	2.64	2.69	2.73	2.77	2.81	2.84	2.87	2.90
35	1.69	2.03	2.22	2.34	2.44	2.52	2.58	2.64	2.69	2.73	2.77	2.80	2.83	2.86	2.89
36	1.69	2.03	2.22	2.34	2.44	2.51	2.58	2.63	2.68	2.72	2.76	2.80	2.83	2.86	2.88
37	1.69	2.03	2.21	2.34	2.43	2.51	2.57	2.63	2.68	2.72	2.76	2.79	2.82	2.85	2.88
38	1.69	2.03	2.21	2.34	2.43	2.51	2.57	2.63	2.67	2.72	2.75	2.79	2.82	2.85	2.87
39	1.69	2.02	2.21	2.33	2.43	2.50	2.57	2.62	2.67	2.71	2.75	2.78	2.81	2.84	2.87
40	1.68	2.02	2.21	2.33	2.43	2.50	2.56	2.62	2.67	2.71	2.75	2.78	2.81	2.84	2.87
41	1.68	2.02	2.20	2.33	2.42	2.50	2.56	2.62	2.66	2.70	2.74	2.78	2.81	2.84	2.86
42	1.68	2.02	2.20	2.33	2.42	2.50	2.56	2.61	2.66	2.70	2.74	2.77	2.80	2.83	2.86
43	1.68	2.02	2.20	2.32	2.42	2.49	2.56	2.61	2.66	2.70	2.74	2.77	2.80	2.83	2.85
44	1.68	2.02	2.20	2.32	2.42	2.49	2.55	2.61	2.65	2.69	2.73	2.77	2.80	2.82	2.85
45	1.68	2.02	2.20	2.32	2.41	2.49	2.55	2.60	2.65	2.69	2.73	2.76	2.79	2.82	2.85
46	1.68	2.01	2.20	2.32	2.41	2.49	2.55	2.60	2.65	2.69	2.73	2.76	2.79	2.82	2.84
47	1.68	2.01	2.19	2.32	2.41	2.48	2.55	2.60	2.65	2.69	2.72	2.76	2.79	2.82	2.84
48	1.68	2.01	2.19	2.32	2.41	2.48	2.54	2.60	2.64	2.68	2.72	2.75	2.78	2.81	2.84
49	1.68	2.01	2.19	2.31	2.41	2.48	2.54	2.60	2.64	2.68	2.72	2.75	2.78	2.81	2.84
50	1.68	2.01	2.19	2.31	2.40	2.48	2.54	2.59	2.64	2.68	2.72	2.75	2.78	2.81	2.84
60	1.67	2.00	2.18	2.30	2.39	2.46	2.52	2.58	2.62	2.66	2.70	2.73	2.76	2.79	2.81
70	1.67	1.99	2.17	2.29	2.38	2.45	2.51	2.56	2.61	2.65	2.68	2.72	2.75	2.77	2.80
80	1.66	1.99	2.17	2.28	2.37	2.45	2.51	2.56	2.60	2.64	2.67	2.71	2.74	2.76	2.79
90	1.66	1.99	2.16	2.28	2.37	2.44	2.50	2.55	2.59	2.63	2.67	2.70	2.73	2.75	2.78
100	1.66	1.98	2.16	2.28	2.36	2.44	2.49	2.54	2.59	2.63	2.66	2.69	2.72	2.75	2.77

Factor = $t_{(\alpha=1,1-\alpha/k)}$

TABLE 6

VALUES OF t FOR OBTAINING ONE-SIDED 95% POISSON PREDICTION LIMITS FOR k ADDITIONAL SAMPLES GIVEN A BACKGROUND SAMPLE OF SIZE n

Previous n	Number of new measurements (k)															
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
4	6.89	7.04	7.18	7.32	7.45	7.58	7.70	7.82	7.94	8.05	8.16	8.27	8.37	8.47	8.57
5	5.26	5.36	5.44	5.52	5.60	5.67	5.75	5.82	5.88	5.95	6.01	6.08	6.14	6.20	6.25
6	4.53	4.59	4.65	4.72	4.77	4.83	4.88	4.93	4.98	5.03	5.08	5.12	5.16	5.21	5.25
7	4.11	4.17	4.22	4.27	4.32	4.36	4.40	4.45	4.49	4.52	4.56	4.60	4.63	4.66	4.70
8	3.85	3.90	3.95	3.99	4.03	4.07	4.10	4.14	4.17	4.21	4.24	4.27	4.30	4.33	4.36
9	3.68	3.72	3.76	3.80	3.83	3.87	3.90	3.93	3.96	3.99	4.02	4.05	4.07	4.10	4.12
10	3.55	3.59	3.62	3.66	3.69	3.72	3.75	3.78	3.81	3.83	3.86	3.88	3.91	3.93	3.96
11	3.45	3.48	3.52	3.55	3.58	3.61	3.64	3.67	3.69	3.72	3.74	3.76	3.78	3.81	3.83
12	3.37	3.40	3.44	3.47	3.50	3.53	3.55	3.58	3.60	3.62	3.65	3.67	3.69	3.71	3.73
13	3.31	3.34	3.37	3.40	3.43	3.45	3.48	3.50	3.53	3.55	3.57	3.59	3.61	3.63	3.65
14	3.26	3.29	3.32	3.35	3.37	3.40	3.42	3.45	3.47	3.49	3.51	3.53	3.55	3.57	3.58
15	3.21	3.24	3.27	3.30	3.33	3.35	3.37	3.40	3.42	3.44	3.46	3.48	3.49	3.51	3.53
16	3.18	3.21	3.23	3.26	3.29	3.31	3.33	3.35	3.37	3.39	3.41	3.43	3.45	3.47	3.48
17	3.15	3.17	3.20	3.23	3.25	3.27	3.30	3.32	3.34	3.36	3.38	3.39	3.41	3.43	3.44
18	3.12	3.15	3.17	3.20	3.22	3.24	3.27	3.29	3.31	3.33	3.34	3.36	3.38	3.39	3.41
19	3.09	3.12	3.15	3.17	3.20	3.22	3.24	3.26	3.28	3.30	3.32	3.33	3.35	3.36	3.38
20	3.07	3.10	3.13	3.15	3.17	3.20	3.22	3.24	3.26	3.27	3.29	3.31	3.32	3.34	3.35
21	3.06	3.08	3.11	3.13	3.15	3.17	3.19	3.21	3.23	3.25	3.27	3.28	3.30	3.32	3.33
22	3.04	3.06	3.09	3.11	3.13	3.16	3.18	3.20	3.21	3.23	3.25	3.26	3.28	3.29	3.31
23	3.02	3.05	3.07	3.10	3.12	3.14	3.16	3.18	3.20	3.21	3.23	3.25	3.26	3.28	3.29
24	3.01	3.03	3.06	3.08	3.10	3.12	3.14	3.16	3.18	3.20	3.21	3.23	3.25	3.26	3.28
25	3.00	3.02	3.05	3.07	3.09	3.11	3.13	3.15	3.17	3.18	3.20	3.21	3.23	3.24	3.26
26	2.99	3.01	3.03	3.05	3.08	3.10	3.12	3.14	3.15	3.17	3.18	3.20	3.21	3.23	3.24
27	2.98	3.00	3.02	3.04	3.07	3.09	3.11	3.12	3.14	3.16	3.17	3.19	3.20	3.22	3.23
28	2.96	2.99	3.01	3.04	3.06	3.08	3.09	3.11	3.13	3.15	3.16	3.18	3.19	3.20	3.22
29	2.96	2.98	3.00	3.03	3.05	3.07	3.09	3.10	3.12	3.14	3.15	3.16	3.18	3.19	3.21
30	2.95	2.97	3.00	3.02	3.04	3.06	3.08	3.09	3.11	3.13	3.14	3.15	3.17	3.18	3.19
31	2.94	2.96	2.99	3.01	3.03	3.05	3.07	3.08	3.10	3.12	3.13	3.14	3.16	3.17	3.18
32	2.93	2.96	2.98	3.00	3.02	3.04	3.06	3.08	3.09	3.11	3.12	3.13	3.15	3.16	3.18
33	2.93	2.95	2.97	2.99	3.01	3.03	3.05	3.07	3.09	3.10	3.12	3.13	3.14	3.15	3.17
34	2.92	2.94	2.97	2.99	3.01	3.03	3.04	3.06	3.08	3.09	3.11	3.12	3.13	3.14	3.16
35	2.91	2.94	2.96	2.98	3.00	3.02	3.04	3.06	3.08	3.09	3.11	3.12	3.14	3.15	3.16
36	2.91	2.93	2.95	2.98	3.00	3.01	3.03	3.05	3.07	3.09	3.10	3.12	3.13	3.14	3.16
37	2.90	2.93	2.95	2.97	2.99	3.01	3.03	3.04	3.06	3.07	3.08	3.10	3.11	3.12	3.14
38	2.90	2.92	2.94	2.97	2.98	3.00	3.02	3.04	3.05	3.07	3.08	3.09	3.10	3.12	3.13
39	2.89	2.92	2.94	2.96	2.98	3.00	3.02	3.03	3.05	3.06	3.08	3.09	3.10	3.11	3.12
40	2.89	2.91	2.94	2.96	2.98	2.99	3.01	3.03	3.04	3.06	3.07	3.08	3.09	3.11	3.12
41	2.89	2.91	2.93	2.96	2.97	2.99	3.01	3.02	3.04	3.05	3.07	3.08	3.09	3.10	3.11
42	2.88	2.91	2.93	2.96	2.97	2.98	3.00	3.02	3.03	3.05	3.06	3.08	3.09	3.10	3.11
43	2.88	2.90	2.92	2.94	2.96	2.98	3.00	3.01	3.03	3.05	3.06	3.08	3.09	3.10	3.12
44	2.88	2.90	2.92	2.94	2.96	2.98	2.99	3.01	3.03	3.04	3.06	3.07	3.09	3.10	3.11
45	2.87	2.89	2.92	2.94	2.96	2.97	2.99	3.01	3.02	3.04	3.05	3.07	3.08	3.10	3.11
46	2.87	2.89	2.91	2.93	2.95	2.97	2.99	3.00	3.02	3.03	3.05	3.06	3.08	3.09	3.10
47	2.87	2.89	2.91	2.93	2.95	2.97	2.98	3.00	3.02	3.03	3.04	3.06	3.07	3.09	3.10
48	2.86	2.89	2.91	2.93	2.95	2.96	2.98	3.00	3.01	3.03	3.04	3.06	3.07	3.08	3.10
49	2.86	2.88	2.90	2.92	2.94	2.96	2.98	2.99	3.01	3.02	3.04	3.05	3.07	3.08	3.09
50	2.86	2.88	2.90	2.92	2.94	2.96	2.97	2.99	3.01	3.02	3.03	3.05	3.06	3.08	3.09
60	2.84	2.86	2.88	2.90	2.92	2.93	2.95	2.97	2.98	3.00	3.01	3.02	3.04	3.05	3.06
70	2.83	2.84	2.86	2.88	2.90	2.92	2.93	2.96	2.96	2.98	2.99	3.00	3.02	3.03	3.04
80	2.81	2.83	2.85	2.87	2.89	2.90	2.92	2.94	2.96	2.97	2.98	2.99	3.00	3.02	3.03
90	2.80	2.82	2.84	2.86	2.88	2.90	2.91	2.93	2.94	2.96	2.97	2.98	2.99	3.00	3.02
100	2.79	2.82	2.84	2.85	2.87	2.89	2.90	2.92	2.93	2.95	2.96	2.97	2.98	2.99	3.00

Factor = $t_{(\alpha=1.1-\alpha/k)}$

TABLE 7

VALUES OF k FOR OBTAINING ONE-SIDED 95% POISSON PREDICTION LIMITS FOR k ADDITIONAL SAMPLES GIVEN A BACKGROUND SAMPLE OF SIZE n

Previous n	Number of new measurements (k)															
	30	35	40	45	50	55	60	65	70	75	80	85	90	95	1(
4	8.87	9.04	9.46	9.85	10.21	10.54	10.87	11.17	11.45	11.72	11.98	12.23	12.47	12.70	12
5	6.26	6.53	6.76	6.97	7.17	7.36	7.53	7.69	7.84	7.98	8.12	8.25	8.38	8.50	8
6	5.25	5.44	5.60	5.76	5.89	6.02	6.14	6.25	6.35	6.45	6.54	6.63	6.71	6.79	6.8
7	4.70	4.85	4.98	5.10	5.21	5.31	5.40	5.48	5.56	5.64	5.71	5.78	5.84	5.90	5.9
8	4.36	4.48	4.59	4.69	4.78	4.87	4.94	5.02	5.08	5.14	5.20	5.26	5.31	5.36	5.4
9	4.12	4.23	4.33	4.42	4.50	4.57	4.64	4.70	4.76	4.81	4.86	4.91	4.96	5.00	5.0
10	3.96	4.06	4.16	4.23	4.30	4.36	4.42	4.48	4.53	4.58	4.62	4.67	4.71	4.74	4.7
11	3.83	3.93	4.00	4.08	4.14	4.20	4.26	4.31	4.36	4.40	4.44	4.48	4.52	4.55	4.5
12	3.73	3.82	3.89	3.96	4.02	4.08	4.13	4.18	4.22	4.26	4.30	4.34	4.37	4.41	4.4
13	3.65	3.73	3.81	3.87	3.93	3.98	4.03	4.08	4.13	4.15	4.19	4.23	4.26	4.29	4.3
14	3.58	3.66	3.73	3.80	3.85	3.90	3.96	3.99	4.03	4.07	4.10	4.13	4.16	4.19	4.2
15	3.53	3.61	3.67	3.73	3.79	3.84	3.88	3.92	3.96	3.99	4.03	4.06	4.09	4.11	4.1
16	3.48	3.56	3.62	3.68	3.73	3.78	3.82	3.86	3.90	3.93	3.96	3.99	4.02	4.05	4.0
17	3.44	3.52	3.58	3.64	3.69	3.73	3.77	3.81	3.84	3.88	3.91	3.94	3.96	3.99	4.0
18	3.41	3.48	3.54	3.60	3.65	3.69	3.73	3.77	3.80	3.83	3.86	3.89	3.92	3.94	3.9
19	3.38	3.45	3.51	3.56	3.61	3.65	3.69	3.73	3.76	3.79	3.82	3.85	3.87	3.90	3.9
20	3.35	3.42	3.48	3.53	3.58	3.62	3.66	3.69	3.73	3.76	3.79	3.81	3.84	3.86	3.8
21	3.33	3.40	3.46	3.51	3.55	3.59	3.63	3.66	3.70	3.73	3.75	3.78	3.80	3.83	3.8
22	3.31	3.38	3.43	3.48	3.53	3.57	3.60	3.64	3.67	3.70	3.73	3.75	3.77	3.80	3.8
23	3.29	3.35	3.41	3.46	3.50	3.54	3.58	3.61	3.64	3.67	3.70	3.73	3.75	3.77	3.8
24	3.27	3.34	3.39	3.44	3.48	3.52	3.56	3.59	3.62	3.65	3.68	3.70	3.73	3.75	3.7
25	3.26	3.32	3.38	3.42	3.47	3.50	3.54	3.57	3.60	3.63	3.66	3.68	3.70	3.73	3.7
26	3.24	3.31	3.36	3.41	3.45	3.49	3.52	3.55	3.58	3.61	3.64	3.66	3.68	3.70	3.7
27	3.23	3.29	3.35	3.39	3.43	3.47	3.51	3.54	3.57	3.59	3.62	3.64	3.67	3.69	3.7
28	3.22	3.28	3.33	3.38	3.42	3.46	3.49	3.52	3.55	3.58	3.60	3.63	3.66	3.67	3.6
29	3.21	3.27	3.32	3.37	3.41	3.44	3.48	3.51	3.54	3.56	3.59	3.61	3.63	3.65	3.6
30	3.20	3.26	3.31	3.36	3.40	3.43	3.47	3.50	3.52	3.55	3.58	3.60	3.62	3.64	3.6
31	3.19	3.25	3.30	3.34	3.38	3.42	3.45	3.48	3.51	3.54	3.56	3.58	3.61	3.63	3.6
32	3.18	3.24	3.29	3.33	3.37	3.41	3.44	3.47	3.50	3.53	3.55	3.57	3.59	3.61	3.6
33	3.17	3.23	3.28	3.33	3.37	3.40	3.43	3.46	3.49	3.52	3.54	3.56	3.58	3.60	3.6
34	3.16	3.22	3.27	3.32	3.36	3.39	3.42	3.45	3.48	3.51	3.53	3.55	3.57	3.59	3.6
35	3.16	3.21	3.26	3.31	3.35	3.38	3.42	3.44	3.47	3.50	3.52	3.54	3.56	3.58	3.6
36	3.15	3.21	3.26	3.30	3.34	3.37	3.41	3.44	3.46	3.49	3.51	3.53	3.55	3.57	3.5
37	3.14	3.20	3.25	3.29	3.33	3.37	3.40	3.43	3.45	3.48	3.50	3.52	3.54	3.56	3.5
38	3.14	3.19	3.24	3.29	3.32	3.36	3.39	3.42	3.45	3.47	3.49	3.52	3.54	3.56	3.5
39	3.13	3.19	3.24	3.28	3.32	3.35	3.38	3.41	3.44	3.46	3.49	3.51	3.53	3.55	3.5
40	3.13	3.18	3.23	3.27	3.31	3.35	3.38	3.41	3.43	3.46	3.48	3.50	3.52	3.54	3.5
41	3.12	3.18	3.23	3.27	3.31	3.34	3.37	3.40	3.43	3.45	3.47	3.49	3.51	3.53	3.5
42	3.12	3.17	3.22	3.26	3.30	3.33	3.37	3.39	3.42	3.44	3.47	3.49	3.51	3.53	3.5
43	3.11	3.17	3.22	3.26	3.30	3.33	3.36	3.39	3.41	3.44	3.46	3.48	3.50	3.52	3.5
44	3.11	3.16	3.21	3.25	3.29	3.32	3.35	3.38	3.41	3.43	3.45	3.48	3.49	3.51	3.5
45	3.10	3.16	3.21	3.25	3.29	3.32	3.35	3.38	3.40	3.43	3.45	3.47	3.49	3.51	3.5
46	3.10	3.15	3.20	3.24	3.28	3.31	3.34	3.37	3.40	3.42	3.44	3.46	3.48	3.50	3.5
47	3.10	3.15	3.20	3.24	3.28	3.31	3.34	3.37	3.39	3.42	3.44	3.46	3.48	3.50	3.5
48	3.09	3.15	3.19	3.24	3.27	3.31	3.34	3.36	3.39	3.41	3.43	3.45	3.47	3.49	3.5
49	3.09	3.14	3.19	3.23	3.27	3.30	3.33	3.36	3.38	3.41	3.43	3.45	3.47	3.49	3.5
50	3.09	3.14	3.19	3.23	3.26	3.30	3.33	3.35	3.38	3.40	3.43	3.45	3.47	3.49	3.5
60	3.06	3.11	3.16	3.20	3.23	3.27	3.30	3.32	3.35	3.37	3.39	3.41	3.43	3.45	3.4
70	3.04	3.09	3.14	3.18	3.21	3.24	3.27	3.30	3.32	3.34	3.37	3.39	3.41	3.43	3.4
80	3.03	3.08	3.12	3.16	3.20	3.23	3.26	3.28	3.31	3.33	3.35	3.37	3.39	3.40	3.4
90	3.02	3.07	3.11	3.15	3.18	3.21	3.24	3.27	3.29	3.31	3.33	3.35	3.37	3.38	3.4
100	3.01	3.06	3.10	3.14	3.17	3.20	3.23	3.26	3.28	3.30	3.32	3.34	3.36	3.38	3.3

Factor = $f_{(n-1,1-\alpha/k)}$

TABLE 8

Hypothetical Ground-Water Monitoring Results for Two Background Wells Monitored Quarterly for Two Years (reported in $\mu g/l$)

Well	Quarter	Year	Chromium	Lead	Benzene	Toluene
1	1	87	20	50	nd	nd
1	2	87	nd	60	nd	nd
1	3	87	40	70	nd	nd
1	4	87	30	40	nd	nd
1	1	88	nd	30	nd	nd
1	2	88	nd	20	nd	nd
1	3	88	nd	10	nd	20
1	4	88	50	15	nd	nd
2	1	87	70	30	nd	nd
2	2	87	nd	25	nd	nd
2	3	87	nd	40	nd	nd
2	4	87	nd	16	nd	nd
2	1	88	nd	18	nd	nd
2	2	88	40	19	nd	nd
2	3	88	20	23	nd	nd
2	4	88	nd	35	nd	nd
Detection Frequencey			44%	100%	0%	6%
$\bar{x}$ (detected)			38.57	31.31	-	-
s (detected)			17.73	17.04	-	-

Statistical Prediction Intervals for the Evaluation of Ground-Water Quality

by Robert D. Gibbons

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ABSTRACT

Factors for a normal distribution are given such that one may be 99% confident that the two-sided prediction interval $\bar{x} \pm ts$ or the one-sided prediction interval $\bar{x} + ts$ will contain all of the k future values, where $\bar{x}$ and s are the sample mean and standard deviation obtained from n previous values. In the context of ground-water monitoring, the future samples may represent new monitoring values at each of k downgradient wells, and the n previous values might be the historical monitoring results for one or more upgradient wells. The Tables provided in this paper allow the computation of one-sided and two-sided 99% prediction intervals for previous sample sizes of $n = 4$ to 100 and future samples of $k = 1$ to 100. Modification of these intervals for log-normally distributed data is also presented.

1. INTRODUCTION

The principal objective of ground-water monitoring at hazardous waste disposal facilities is to empirically determine if on-site chemical waste is migrating off-site in ground water. The principal method of ground-water monitoring involves a comparison of specific chemical constituents of ground water upgradient of the site with similarly collected and analyzed samples downgradient of the site. The null hypothesis of interest in such monitoring programs is that of no difference in chemical composition of ground water upgradient and downgradient of the facility. The logic in such a comparison is that presumably, the upgradient wells monitor ground water that is unaffected by the waste disposal facility, whereas the downgradient wells are in the path of ground water that flows underneath the site, and therefore should provide an early warning system for any potential off-site migration of hazardous waste. The validity of this monitoring procedure *is not* the focus of this paper. The development of a statistically rigorous hypothesis testing strategy *is* the focus of this paper.

If ground water were in the form of a well-mixed underground river or lake that spanned the entire area of the site, the most direct approach to testing for upgradient versus downgradient differences would be to obtain estimates of means and variances for individual compounds for all upgradient wells and similar estimates for all downgradient wells. If the variances of these two distributions were reasonably similar, the measurements independent (*i.e.*, not replicate measurements obtained from the same sample), and the compounds in question had approximately normal (*i.e.*, Gaussian) distributions, one could readily compare the two distributions using Student's t-statistic for each indicator parameter separately, or if a sufficient number of monitoring wells were available, all of the indicator parameters could be

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t-statistic (Anderson, 1958)]. Alternatively, if the assumption of homogeneity of variance could not be supported, one could use an unequal variance t-statistic such as Cochran's approximation to the Behrens-Fisher t-statistic (Snedecor and Cochran, 1980).

From a statistical perspective it is unfortunate that the ground-water lake or river example falls considerably short of reality. Ground water occurs in geologically discrete aquifers which generally move extremely slowly (*i.e.*, inches per year) and in rare cases can exhibit a plume-like projection, such that only localized areas of the downgradient geology may exhibit contamination. In light of this, pooling information obtained from downgradient wells, some of which may be contaminated and some of which may be perfectly normal, does not seem sensible.

If we cannot estimate a mean and variance for a collection of downgradient well measurements on a particular occasion, we cannot compute a t-statistic. The reason for this is that a t-statistic is appropriate for the comparison of two mean values; however, if each downgradient well is examined individually, its measurement is not the mean of anything, it is simply a single new observation which must in turn be compared to a historical upgradient sample of measurements in order to assess its significance. Stated statistically, we desire an interval or range of values that will have high probability of containing all new monitoring observations. If the monitoring program involves multiple wells, we must construct an interval that will include all of the k future observations, where k is the number of wells that are to be evaluated on the next monitoring event. Intervals of this type are called "prediction intervals" and need to be distinguished both from a confidence interval on an unknown distribution parameter (*e.g.*, a confidence interval of a mean value), and from a tolerance interval which contains the values of a specified proportion of the population with a certain level of confidence. Hahn (1970) illustrates this distinction by providing an example of the typical astronaut's problem. "An astronaut who has been assigned to a limited number of space flights is not very interested in what will happen on the average in the population of all space flights, of which his happens to be a random sample, or even in what will happen in 99% of the population of such space flights. His main interest is in the worst that may happen in the one, or three, or five flights in which [illegible] on the average in the popula[tion] of all space flights represents a confidence inte[rval] wh[ich] will happen in 99% of the population of space flights is a tolerance interval, and what wil[l] happen in the next one, or three, or five space flights represents a prediction interval.

2. STATISTICAL DEVELOPMENT

Our objective is to define an interval

$$\bar{x} \pm r(k, n; 1 - \alpha)s$$

that will contain the values of all k future measurements, where $\bar{x}$ and s are the sample mean and standard deviation calculated from the values $x_1, \ldots, x_n$ of n previous measurements; that is,

$$\bar{x} = \sum_{i=1}^{n} x_i/n$$

$$s^2 = \sum_{i=1}^{n} (x_i - \bar{x})^2/(n - 1).$$

The original n observations and the additional k samples are assumed to be independent random samples (*i.e.*, not analytical replicates) from the same normal distribution. For the case of a single new observation, Wilks (1941) showed that when sampling from a $N(\mu, \sigma^2)$ with μ and σ^2 unknown the coverage c of the interval

$$c = \int_{\bar{x}-rs}^{\bar{x}+rs} \sqrt{2\pi\sigma^2} \exp\{-\frac{1}{2\sigma^2}(x - \mu)^2\}\, dy$$

will on the average be $1 - \alpha$, if and only if

$$r = \sqrt{1 + 1/n}\; t_{[n-1;\alpha/2]}$$

where $t_{[n-1;\alpha/2]}$ is the $100(1 - \alpha)\%$ point of "Student's" t-distribution with $n - 1$ degrees of freedom.

Chew (1968) extended this result to the case of k future observations using an approximate conservative method for obtaining prediction intervals based on the Bonferroni inequality (Miller, 1966). This approximation leads to the $100(1 - \alpha)\%$ two-sided prediction limit:

$$\bar{x} \pm \sqrt{1 + 1/n}\; t_{[n-1;\alpha/2k]}\, s$$

and the $100(1 - \alpha)\%$ one-sided upper prediction limit:

$$\bar{x} + \sqrt{1 + 1/n}\; t_{[n-1;\alpha/k]}\, s$$

Hahn (1969 and 1970) compared results u[illegible]

using numerical quadrature and found the approximation to be satisfactory for practical purposes. Comparison of values in Tables 1-3, which provide values of $r(k, n; .99)$ for $n = 4$ to 100 and $k = 1$ to 100 for one-sided intervals, and Tables 4-6 for the corresponding two-sided intervals reveal that on the average, the bias is less than 1% with a maximum deviation of 7% for $n = 4$ and $k = 1$. In fact, for $n > 4$ the bias is never greater than 1% regardless of k. The small bias observed for $n = 4$ is always an underestimate; therefore, the approximation is not be used in practice. For example, the exact one-tailed result for $n = 15$ and $k = 4$ is $r(4, 15; \quad) = 3.42$, and the approximate value given in Table 1 is 3.43. Using this example in a practical application, we would compute the 99% upper prediction limit as $\bar{x} + 3.43s$, where in this example, $\bar{x}$ and s would be computed on 15 background (upgradient) measurements, and each of the four new monitoring (downgradient) measurements would simply be compared to this limit value.

Table 1. Factors for Obtaining One-Sided 99% Prediction Limits for k Additional Samples Given a Background Sample of Size n

Previous n	Number of new measurements (k)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	4.70	5.81	6.62	7.26	7.69	7.86	8.17	8.45	8.71	8.94	9.15	9.35	9.53	9.70	9.86
5	3.96	4.77	5.38	5.88	6.06	6.33	6.44	6.63	6.81	6.97	7.11	7.24	7.37	7.48	7.59
6	3.57	4.23	4.63	4.95	5.17	5.37	5.54	5.69	5.83	5.96	6.08	6.16	6.26	6.35	6.43
7	3.32	3.89	4.24	4.48	4.69	4.86	5.00	5.13	5.24	5.34	5.43	5.52	5.60	5.67	5.74
8	3.16	3.67	3.98	4.20	4.38	4.52	4.65	4.75	4.85	4.94	5.01	5.09	5.16	5.22	5.28
9	3.04	3.51	3.79	3.99	4.15	4.28	4.39	4.49	4.58	4.66	4.73	4.79	4.85	4.91	4.96
10	2.95	3.39	3.65	3.84	3.98	4.10	4.21	4.30	4.37	4.45	4.51	4.57	4.62	4.68	4.72
11	2.88	3.30	3.54	3.72	3.86	3.97	4.08	4.14	4.23	4.28	4.34	4.40	4.45	4.50	4.54
12	2.82	3.22	3.46	3.63	3.75	3.86	3.96	4.03	4.09	4.16	4.21	4.26	4.31	4.36	4.40
13	2.78	3.16	3.39	3.54	3.67	3.77	3.86	3.93	3.99	4.06	4.11	4.16	4.20	4.24	4.28
14	2.74	3.11	3.33	3.48	3.60	3.70	3.78	3.85	3.91	3.97	4.02	4.07	4.11	4.15	4.19
15	2.71	3.07	3.28	3.43	3.54	3.63	3.71	3.78	3.84	3.90	3.95	3.99	4.03	4.07	4.11
16	2.68	3.03	3.24	3.38	3.49	3.58	3.66	3.72	3.78	3.84	3.88	3.93	3.97	4.00	4.04
17	2.66	3.00	3.20	3.34	3.45	3.54	3.61	3.68	3.73	3.78	3.83	3.87	3.91	3.95	3.98
18	2.64	2.97	3.17	3.31	3.41	3.50	3.57	3.63	3.69	3.74	3.78	3.82	3.86	3.89	3.93
19	2.62	2.95	3.14	3.28	3.38	3.46	3.53	3.60	3.66	3.70	3.74	3.78	3.82	3.85	3.88
20	2.60	2.93	3.12	3.25	3.35	3.43	3.50	3.56	3.61	3.66	3.70	3.74	3.78	3.81	3.84
21	2.59	2.91	3.10	3.23	3.32	3.41	3.47	3.53	3.58	3.63	3.67	3.71	3.75	3.78	3.81
22	2.57	2.89	3.08	3.20	3.30	3.38	3.45	3.51	3.56	3.60	3.64	3.68	3.71	3.75	3.78
23	2.56	2.88	3.06	3.18	3.28	3.36	3.43	3.48	3.53	3.58	3.62	3.65	3.69	3.72	3.75
24	2.55	2.86	3.04	3.17	3.26	3.34	3.40	3.46	3.51	3.55	3.59	3.63	3.66	3.69	3.72
25	2.54	2.85	3.03	3.15	3.24	3.32	3.38	3.44	3.49	3.53	3.57	3.61	3.64	3.67	3.70
26	2.53	2.84	3.01	3.14	3.23	3.30	3.37	3.42	3.47	3.51	3.55	3.59	3.62	3.65	3.68
27	2.52	2.83	3.00	3.12	3.21	3.29	3.36	3.41	3.46	3.50	3.53	3.57	3.60	3.63	3.66
28	2.52	2.82	2.99	3.11	3.20	3.27	3.34	3.39	3.44	3.48	3.52	3.55	3.58	3.61	3.64
29	2.51	2.81	2.98	3.10	3.19	3.26	3.33	3.38	3.43	3.46	3.50	3.54	3.57	3.60	3.63
30	2.50	2.80	2.97	3.09	3.18	3.25	3.31	3.36	3.41	3.45	3.49	3.52	3.55	3.58	3.61
31	2.50	2.79	2.96	3.08	3.17	3.24	3.30	3.35	3.40	3.44	3.47	3.51	3.54	3.57	3.59
32	2.49	2.79	2.96	3.07	3.16	3.23	3.29	3.34	3.39	3.43	3.46	3.50	3.53	3.55	3.58
33	2.49	2.78	2.94	3.06	3.15	3.22	3.28	3.33	3.37	3.41	3.45	3.48	3.51	3.54	3.57
34	2.48	2.77	2.94	3.05	3.14	3.21	3.27	3.32	3.36	3.40	3.44	3.47	3.50	3.53	3.56
35	2.48	2.77	2.93	3.04	3.13	3.20	3.26	3.31	3.35	3.39	3.43	3.46	3.49	3.52	3.54
36	2.47	2.76	2.92	3.04	3.12	3.19	3.25	3.30	3.35	3.39	3.42	3.45	3.48	3.51	3.53
37	2.47	2.76	2.92	3.03	3.12	3.19	3.24	3.29	3.34	3.38	3.41	3.44	3.47	3.50	3.53
38	2.46	2.75	2.91	3.02	3.11	3.18	3.24	3.29	3.33	3.37	3.40	3.44	3.46	3.49	3.52
39	2.46	2.75	2.91	3.02	3.10	3.17	3.23	3.28	3.32	3.36	3.40	3.43	3.46	3.48	3.51
40	2.46	2.74	2.90	3.01	3.10	3.17	3.22	3.27	3.31	3.35	3.39	3.42	3.45	3.47	3.50
41	2.45	2.74	2.90	3.01	3.09	3.16	3.22	3.27	3.31	3.35	3.38	3.41	3.44	3.47	3.49
42	2.45	2.73	2.89	3.00	3.09	3.16	3.21	3.26	3.30	3.34	3.37	3.41	3.43	3.46	3.48
43	2.45	2.73	2.89	3.00	3.08	3.15	3.20	3.25	3.30	3.33	3.37	3.40	3.43	3.45	3.48
44	2.44	2.73	2.88	2.99	3.08	3.14	3.20	3.25	3.29	3.33	3.36	3.39	3.42	3.45	3.47
45	2.44	2.72	2.88	2.99	3.07	3.14	3.19	3.24	3.28	3.32	3.36	3.39	3.41	3.44	3.46
46	2.44	2.72	2.88	2.98	3.07	3.13	3.19	3.24	3.28	3.32	3.35	3.38	3.41	3.43	3.46
47	2.44	2.72	2.87	2.98	3.06	3.13	3.18	3.23	3.27	3.31	3.34	3.38	3.40	3.43	3.45
48	2.43	2.71	2.87	2.98	3.06	3.12	3.18	3.23	3.27	3.31	3.34	3.37	3.40	3.42	3.45
49	2.43	2.71	2.86	2.97	3.06	3.12	3.18	3.22	3.26	3.30	3.34	3.37	3.39	3.42	3.44
50	2.43	2.71	2.86	2.97	3.05	3.12	3.17	3.22	3.26	3.30	3.33	3.36	3.39	3.41	3.44
60	2.41	2.68	2.84	2.94	3.02	3.08	3.14	3.18	3.22	3.26	3.29	3.32	3.35	3.37	3.40
70	2.40	2.67	2.82	2.92	3.00	3.06	3.12	3.16	3.20	3.24	3.27	3.30	3.32	3.35	3.37
80	2.39	2.66	2.80	2.91	2.98	3.05	3.10	3.14	3.18	3.22	3.25	3.28	3.30	3.33	3.35
90	2.38	2.65	2.79	2.89	2.97	3.03	3.08	3.13	3.17	3.20	3.23	3.26	3.29	3.31	3.33
100	2.38	2.64	2.78	2.88	2.96	3.02	3.07	3.12	3.16	3.19	3.22	3.25	3.27	3.30	3.32

Factor $t_{n-1;1-\alpha/k}\sqrt{1+1/n}$

4	10.01	10.16	10.30	10.43	10.55	10.67	10.78	10.90	11.00	11.11	11.21	11.30	11.40	11.49	11.57	
5	7.70	7.79	[illegible]	7.97	8.05	8.14	8.22	8.29	8.36	[illegible]	8.50	8.56	8.62	8.68	8.74	
6	6.61	6.68		6.78	6.79	6.85	6.90	6.96	7.02		7.12	7.17	7.21	7.26	7.30	
7	5.90	5.96	6.01	6.06	6.09	6.14	6.18	6.21	6.25	6.28	6.30	6.34	6.38	6.41	6.45	
8	5.54	5.59	5.64	5.69	5.73	5.77	5.81	5.85	5.89	5.92	5.95	5.98	6.02	6.05	6.09	
9	5.01	5.06	5.10	5.14	5.18	5.21	5.25	5.29	5.32	5.36	5.39	5.42	5.44	5.47	5.50	
10	4.77	4.81	4.85	4.89	4.92	4.96	4.99	5.02	5.05	5.08	5.11	5.14	5.16	5.19	5.21	
11	4.58	4.62	4.66	4.69	4.73	4.76	4.79	4.82	4.84	4.87	4.90	4.92	4.94	4.97	4.99	
12	4.44	4.47	4.51	4.54	4.57	4.60	4.63	4.66	4.68	4.71	4.73	4.75	4.77	4.80	4.82	
13	4.32	4.35	4.38	4.42	4.44	4.47	4.50	4.52	4.55	4.57	4.59	4.62	4.64	4.66	4.68	
14	4.22	4.26	4.28	4.31	4.34	4.37	4.39	4.42	4.44	4.46	4.48	4.50	4.52	4.54	4.56	
15	4.14	4.17	4.20	4.23	4.25	4.28	4.30	4.33	4.35	4.37	4.39	4.41	4.43	4.45	4.46	
16	4.07	4.10	4.13	4.15	4.18	4.20	4.23	4.25	4.27	4.29	4.31	4.33	4.35	4.37	4.38	
17	4.01	4.04	4.07	4.09	4.12	4.14	4.16	4.18	4.20	4.22	4.24	4.26	4.28	4.30	4.31	
18	3.96	3.99	4.01	4.04	4.06	4.08	4.11	4.13	4.15	4.17	4.18	4.20	4.22	4.24	4.25	
19	3.91	3.94	3.97	3.99	4.01	4.04	4.06	4.08	4.10	4.11	4.13	4.15	4.17	4.18	4.20	
20	3.87	3.90	3.92	3.95	3.97	3.99	4.01	4.03	4.05	4.07	4.09	4.11	4.12	4.14	4.15	
21	3.84	3.86	3.89	3.91	3.93	3.96	3.97	3.99	4.01	4.03	4.05	4.06	4.08	4.09	4.11	
22	3.80	3.83	3.85	3.88	3.90	3.92	3.94	3.96	3.98	4.00	4.01	4.03	4.04	4.06	4.07	
23	3.77	3.80	3.82	3.85	3.87	3.89	3.91	3.93	3.95	3.96	3.98	4.00	4.01	4.02	4.04	
24	3.75	3.77	3.80	3.82	3.84	3.86	3.88	3.90	3.92	3.93	3.95	3.97	3.98	3.99	4.01	
25	3.73	3.75	3.77	3.79	3.82	3.84	3.85	3.87	3.89	3.91	3.92	3.94	3.95	3.97	3.98	
26	3.70	3.73	3.75	3.77	3.79	3.81	3.83	3.85	3.87	3.88	3.90	3.91	3.93	3.94	3.95	
27	3.68	3.71	3.73	3.75	3.77	3.79	3.81	3.83	3.84	3.86	3.87	3.89	3.90	3.92	3.93	
28	3.66	3.69	3.71	3.73	3.75	3.77	3.79	3.81	3.82	3.84	3.86	3.87	3.88	3.90	3.91	
29	3.65	3.67	3.69	3.71	3.73	3.75	3.77	3.79	3.80	3.82	3.84	3.85	3.87	3.88	3.89	
30	3.63	3.66	3.68	3.70	3.72	3.74	3.75	3.77	3.79	3.80	3.82	3.83	3.85	3.86	3.87	
31	3.62	3.64	3.66	3.68	3.70	3.73	3.74	3.76	3.77	3.79	3.80	3.82	3.83	3.85	3.86	
32	3.60	3.63	3.65	3.67	3.69	3.71	3.73	3.74	3.76	3.77	3.79	3.80	3.81	3.83	3.84	
33	3.59	3.61	3.64	3.66	3.67	3.69	3.71	3.73	3.74	3.76	3.77	3.79	3.80	3.81	3.83	
34	3.58	3.60	3.62	3.64	3.66	3.68	3.70	3.71	3.73	3.74	3.76	3.77	3.79	3.80	3.81	
35	3.57	3.59	3.61	3.63	3.65	3.67	3.68	3.70	3.72	3.73	3.74	3.76	3.77	3.78	3.80	
36	3.56	3.58	3.60	3.62	3.64	3.66	3.67	3.69	3.71	3.72	3.73	3.75	3.76	3.77	3.78	
37	3.55	3.57	3.59	3.61	3.63	3.65	3.66	3.68	3.69	3.71	3.72	3.73	3.75	3.76	3.77	
38	3.54	3.56	3.58	3.60	3.62	3.64	3.65	3.67	3.68	3.70	3.71	3.72	3.74	3.75	3.76	
39	3.53	3.55	3.57	3.59	3.61	3.63	3.64	3.66	3.67	3.69	3.70	3.72	3.73	3.74	3.75	
40	3.52	3.54	3.56	3.58	3.60	3.62	3.63	3.65	3.67	3.68	3.69	3.71	3.72	3.73	3.74	
41	3.51	3.54	3.56	3.58	3.59	3.61	3.63	3.64	3.66	3.67	3.68	3.70	3.71	3.72	3.73	
42	3.51	3.53	3.55	3.57	3.59	3.60	3.62	3.63	3.65	3.66	3.67	3.68	3.70	3.71	3.72	
43	3.50	3.52	3.54	3.56	3.58	3.59	3.61	3.63	3.64	3.65	3.66	3.68	3.69	3.70	3.71	
44	3.49	3.51	3.53	3.55	3.57	3.59	3.60	3.62	3.63	3.65	3.67	3.68	3.69	3.71	3.72	
45	3.49	3.51	3.53	3.55	3.56	3.58	3.60	3.61	3.63	3.64	3.66	3.67	3.69	3.70	3.71	
46	3.48	3.50	3.52	3.54	3.56	3.57	3.59	3.61	3.62	3.63	3.65	3.66	3.67	3.68	3.70	
47	3.48	3.50	3.52	3.53	3.55	3.57	3.58	3.60	3.61	3.63	3.64	3.65	3.67	3.68	3.70	
48	3.47	3.49	3.51	3.53	3.55	3.56	3.58	3.59	3.61	3.62	3.63	3.65	3.66	3.67	3.68	
49	3.46	3.48	3.50	3.52	3.54	3.56	3.57	3.59	3.60	3.62	3.63	3.64	3.65	3.66	3.67	
50	3.46	3.48	3.50	3.52	3.53	3.55	3.57	3.58	3.60	3.61	3.62	3.64	3.65	3.66	3.68	
60	3.42	3.44	3.46	3.47	3.49	3.51	3.52	3.54	3.55	3.56	3.58	3.59	3.60	3.61	3.62	
70	3.39	3.41	3.43	3.45	3.46	3.48	3.49	3.51	3.52	3.53	3.54	3.56	3.57	3.58	3.59	
80	3.37	3.39	3.41	3.42	3.44	3.45	3.47	3.48	3.50	3.51	3.52	3.53	3.54	3.55	3.57	
90	3.35	3.37	3.39	3.41	3.42	3.44	3.45	3.47	3.48	3.49	3.50	3.51	3.53	3.54	3.55	
100	3.34	3.36	3.38	3.39	3.41	3.42	3.44	3.45	3.46	3.48	3.49	3.50	3.51	3.52	3.53	

Factor = $t_{(n-1;\,\alpha/2)}\sqrt{1+1/n}$

3. PREDICTION LIMITS FOR THE LOGNORMAL DISTRIBUTION

When data exhibit a few elevated values such that the frequency distribution is "skewed" with a long right tail, estimates based on the assumption of normality do not apply. In practice, transformations of data are used to stabilize variance and bring about normality (Box and Cox, 1964). Perhaps the most commonly used transformation in this situation is the natural log transformation (Aroian, 1941), where x is a lognormal random variable, such that $y = \log_e x \sim N(\mu, \sigma^2)$. When μ and σ^2 are unknown, we may substitute the sample estimates $\bar{y}$ and s^2 where

$$\bar{y} = \sum_{i=1}^{n} \log_e (x_i)/n$$

and $$s^2 = \sum_{i=1}^{n} [\log_e (x_i) - \bar{y}]^2/(n-1).$$

Based on a result obtained by Dahiya and Guttman (1982), the $100(1-\alpha)\%$ prediction interval has the familiar form

$$\exp\{\bar{y} \pm \sqrt{1+1/n}\; t_{[n-1;\,\alpha/2]}\, s\}.$$

In light of this, the values in Tables 1-3 may be used to obtain the one-sided 99% prediction limit

$$\exp\{\bar{y} + r(k, n; .99)\, s\}$$

Similarly, Tables 4–6 may be used to compute the corresponding two-sided 99% prediction limit:

$$\exp(\bar{y} \pm r(k, n; .99)\, s)$$

A note of caution must be raised regarding the use of log transformation in calculating prediction limits. This point is best illustrated by an example. Consider the following data for TOX, and for simplicity let us assume that these measurements were collected from a single upgradient well, quarterly for two years so that s^2 is an unbiased estimate of σ^2.

			TOX	log(TOX)
MW01	1	1985	48	3.87
MW	2	1985	5	1.61
MW01	3	1985	44	3.78
MW01	4	1985	24	3.18
MW01	1	1986	17	2.83
MW01	2	1986	6	1.79
MW01	3	1986	12	2.48
MW01	4	1986	60	4.09
			$\bar{x}$ = 27.00	$\bar{x}$ = 2.96
			s = 20.97	s = 0.95
			n = 8	n = 8

Inspection of the original TOX values reveals a distribution that is skewed to the right; therefore, log

Table 3. Factors for Obtaining One-Sided 99% Prediction Limits for k Additional Samples Given a Background Sample of Size n

Previous n	Number of new measurements (k)														
	20	25	40	45	50	55	60	65	70	75	80	85	90	95	100
4	11.57	11.98	12.34	12.66	12.96	13.23	13.47	13.70	13.91	14.11	14.31	14.49	14.66	14.82	14.98
5	8.74	9.01	9.25	9.46	9.65	9.83	9.99	10.14	10.29	10.42	10.54	10.66	10.77	10.88	10.98
6	7.30	7.51	7.69	7.84	7.99	8.12	8.24	8.35	8.46	8.55	8.64	8.73	8.82	8.90	8.97
7	6.45	6.61	6.76	6.89	7.00	7.11	7.20	7.29	7.38	7.46	7.53	7.60	7.67	7.73	7.79
8	5.89	6.03	6.15	6.26	6.36	6.45	6.53	6.61	6.68	6.74	6.81	6.87	6.93	6.97	7.02
9	5.50	5.62	5.73	5.82	5.91	5.99	6.06	6.13	6.19	6.25	6.30	6.35	6.40	6.45	6.49
10	5.21	5.32	5.42	5.50	5.58	5.65	5.72	5.77	5.83	5.88	5.93	5.98	6.03	6.06	6.10
11	4.99	5.09	5.18	5.26	5.33	5.39	5.45	5.51	5.56	5.60	5.65	5.69	5.73	5.77	5.80
12	4.82	4.91	4.99	5.07	5.13	5.19	5.25	5.30	5.34	5.39	5.43	5.47	5.50	5.54	5.57
13	4.68	4.77	4.84	4.91	4.97	5.03	5.08	5.13	5.17	5.21	5.25	5.28	5.32	5.35	5.38
14	4.56	4.65	4.72	4.78	4.84	4.89	4.94	4.99	5.03	5.07	5.10	5.14	5.17	5.20	5.23
15	4.46	4.54	4.61	4.68	4.73	4.78	4.83	4.87	4.91	4.95	4.98	5.01	5.04	5.07	5.10
16	4.38	4.46	4.53	4.59	4.64	4.69	4.73	4.77	4.81	4.84	4.88	4.91	4.94	4.96	4.99
17	4.31	4.39	4.45	4.51	4.56	4.61	4.65	4.69	4.72	4.76	4.79	4.82	4.85	4.87	4.90
18	4.25	4.32	4.39	4.44	4.49	4.54	4.58	4.61	4.65	4.68	4.71	4.74	4.77	4.79	4.82
19	4.20	4.27	4.33	4.38	4.43	4.47	4.51	4.55	4.58	4.61	4.64	4.67	4.70	4.72	4.75
20	4.15	4.22	4.28	4.33	4.38	4.42	4.46	4.49	4.53	4.56	4.59	4.61	4.64	4.66	4.68
21	4.11	4.18	4.23	4.28	4.33	4.37	4.41	4.44	4.48	4.50	4.53	4.56	4.58	4.61	4.63
22	4.07	4.14	4.19	4.24	4.29	4.33	4.36	4.40	4.43	4.46	4.49	4.51	4.54	4.56	4.58
23	4.04	4.10	4.16	4.21	4.25	4.29	4.32	4.36	4.39	4.42	4.44	4.47	4.49	4.51	4.54
24	4.01	4.07	4.13	4.17	4.21	4.25	4.28	4.32	4.35	4.38	4.41	4.43	4.45	4.48	4.50
25	3.98	4.04	4.09	4.14	4.18	4.22	4.26	4.29	4.32	4.35	4.37	4.40	4.42	4.44	4.46
26	3.96	4.01	4.07	4.11	4.16	4.19	4.23	4.26	4.29	4.31	4.34	4.36	4.39	4.41	4.43
27	3.93	3.99	4.04	4.09	4.13	4.17	4.20	4.23	4.26	4.29	4.31	4.33	4.36	4.38	4.40
28	3.91	3.97	4.02	4.06	4.11	4.14	4.17	4.21	4.23	4.26	4.29	4.31	4.33	4.35	4.37
29	3.89	3.95	4.00	4.04	4.08	4.12	4.15	4.18	4.21	4.24	4.26	4.28	4.31	4.33	4.35
30	3.87	3.93	3.98	4.02	4.06	4.10	4.13	4.16	4.19	4.21	4.24	4.26	4.28	4.30	4.32
31	3.85	3.91	3.96	4.00	4.04	4.08	4.11	4.14	4.17	4.19	4.22	4.24	4.26	4.28	4.30
32	3.84	3.90	3.94	3.99	4.03	4.06	4.09	4.12	4.15	4.17	4.20	4.22	4.24	4.26	4.28
33	3.82	3.88	3.93	3.97	4.01	4.04	4.08	4.10	4.13	4.16	4.18	4.20	4.22	4.24	4.26
34	3.81	3.87	3.91	3.96	3.99	4.03	4.06	4.09	4.11	4.14	4.16	4.18	4.20	4.22	4.24
35	3.80	3.85	3.90	3.94	3.98	4.01	4.04	4.07	4.10	4.12	4.15	4.17	4.19	4.21	4.23
36	3.79	3.84	3.89	3.93	3.97	4.00	4.03	4.06	4.08	4.11	4.13	4.15	4.17	4.19	4.21
37	3.77	3.83	3.88	3.92	3.96	3.99	4.02	4.04	4.07	4.09	4.12	4.14	4.16	4.18	4.20
38	3.76	3.82	3.86	3.90	3.94	3.97	4.00	4.03	4.06	4.08	4.10	4.12	4.14	4.16	4.18
39	3.75	3.81	3.85	3.89	3.93	3.96	3.99	4.02	4.05	4.07	4.09	4.11	4.13	4.15	4.17
40	3.74	3.80	3.84	3.88	3.92	3.95	3.98	4.01	4.03	4.06	4.08	4.10	4.12	4.14	4.15
41	3.73	3.79	3.83	3.87	3.91	3.94	3.97	4.00	4.02	4.05	4.07	4.09	4.11	4.13	4.14
42	3.72	3.78	3.82	3.86	3.90	3.93	3.96	3.99	4.01	4.04	4.06	4.08	4.10	4.11	4.13
43	3.72	3.77	3.82	3.86	3.89	3.92	3.95	3.98	4.00	4.03	4.05	4.07	4.09	4.10	4.12
44	3.71	3.76	3.81	3.85	3.88	3.91	3.94	3.97	3.99	4.02	4.04	4.06	4.08	4.09	4.11
45	3.70	3.75	3.80	3.84	3.87	3.91	3.93	3.96	3.98	4.01	4.03	4.05	4.07	4.08	4.10
46	3.70	3.75	3.79	3.83	3.87	3.90	3.93	3.95	3.98	4.00	4.02	4.04	4.06	4.08	4.09
47	3.69	3.74	3.78	3.82	3.86	3.89	3.92	3.94	3.97	3.99	4.01	4.03	4.05	4.07	4.08
48	3.68	3.73	3.78	3.82	3.85	3.88	3.91	3.94	3.96	3.98	4.00	4.02	4.04	4.06	4.07
49	3.68	3.73	3.77	3.81	3.84	3.88	3.90	3.93	3.95	3.98	4.00	4.01	4.03	4.05	4.07
50	3.67	3.72	3.76	3.80	3.84	3.87	3.90	3.92	3.95	3.97	3.99	4.01	4.03	4.05	4.06
60	3.62	3.67	3.71	3.75	3.78	3.81	3.84	3.87	3.89	3.91	3.93	3.95	3.97	3.98	4.00
70	3.59	3.64	3.68	3.72	3.75	3.78	3.80	3.83	3.85	3.87	3.89	3.91	3.93	3.94	3.96
80	3.57	3.61	3.66	3.69	3.72	3.75	3.78	3.80	3.83	3.84	3.86	3.88	3.89	3.91	3.93
90	3.55	3.60	3.63	3.67	3.70	3.73	3.75	3.78	3.80	3.82	3.84	3.86	3.87	3.89	3.90
100	3.53	3.58	3.61	3.65	3.68	3.71	3.74	3.76	3.78	3.80	3.82	3.84	3.86	3.87	3.89

Factor = $t_{(n-1,1-\alpha/k)}\sqrt{1+1/n}$

Previous	Number of new measurements (k)															
n	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
4	5.81	[illegible]	7.34	8.45	8.94	9.34	9.70	10.01	10.30	[illegible]	10.79	11.00	11.31	11.60	11.87	
5	4.77	[illegible]	6.33	6.63	6.97	7.24	7.48	7.70	7.89	8.06	8.22	8.36	8.50	8.62	8.74	
6	4.33	4.98	5.27	5.49	5.66	6.16	6.25	6.51	6.61	6.79	6.90	7.02	7.13	7.21	7.30	
7	3.89	4.48	4.86	5.13	5.34	5.53	5.67	5.80	5.92	6.08	6.18	6.31	6.20	6.28	6.45	
8	3.67	4.20	4.53	4.76	4.94	5.09	5.22	5.34	5.44	5.53	5.61	5.69	5.76	5.83	5.89	
9	3.61	3.99	4.28	4.49	4.66	4.79	4.91	5.01	5.10	5.18	5.25	5.32	5.38	5.44	5.50	
10	3.39	3.84	4.10	4.30	4.45	4.57	4.68	4.77	4.85	4.92	4.99	5.05	5.11	5.16	5.21	
11	3.20	3.73	3.97	4.14	4.28	4.40	4.50	4.58	4.66	4.73	4.79	4.84	4.89	4.94	4.99	
12	3.23	3.63	3.86	4.03	4.16	4.26	4.36	4.44	4.51	4.57	4.63	4.68	4.73	4.77	4.82	
13	3.16	3.54	3.77	3.93	4.06	4.16	4.24	4.33	4.38	4.44	4.50	4.55	4.59	4.64	4.68	
14	3.11	3.48	3.70	3.86	3.97	4.07	4.15	4.22	4.28	4.34	4.39	4.44	4.48	4.52	4.56	
15	3.07	3.43	3.63	3.78	3.90	3.99	4.07	4.14	4.20	4.26	4.30	4.35	4.39	4.43	4.46	
16	3.03	3.38	3.58	3.73	3.84	3.93	4.00	4.07	4.13	4.18	4.23	4.27	4.31	4.35	4.38	
17	3.00	3.34	3.54	3.68	3.78	3.87	3.95	4.01	4.07	4.12	4.16	4.20	4.24	4.28	4.31	
18	2.97	3.31	3.50	3.63	3.74	3.83	3.90	3.96	4.01	4.06	4.11	4.15	4.18	4.22	4.25	
19	2.96	3.28	3.46	3.60	3.70	3.78	3.85	3.91	3.97	4.01	4.06	4.10	4.13	4.17	4.20	
20	2.93	3.25	3.43	3.56	3.66	3.74	3.81	3.87	3.92	3.97	4.01	4.05	4.09	4.12	4.15	
21	2.91	3.22	3.41	3.53	3.63	3.71	3.78	3.84	3.89	3.93	3.97	4.01	4.05	4.08	4.11	
22	2.89	3.20	3.38	3.51	3.60	3.68	3.75	3.80	3.86	3.90	3.94	3.98	4.01	4.04	4.07	
23	2.88	3.18	3.36	3.48	3.58	3.65	3.72	3.77	3.82	3.87	3.91	3.94	3.98	4.01	4.04	
24	2.86	3.17	3.34	3.46	3.55	3.63	3.69	3.75	3.80	3.84	3.88	3.92	3.95	3.98	4.01	
25	2.85	3.15	3.32	3.44	3.53	3.61	3.67	3.73	3.77	3.82	3.85	3.89	3.92	3.95	3.98	
26	2.84	3.14	3.30	3.42	3.51	3.59	3.65	3.70	3.75	3.79	3.83	3.87	3.90	3.93	3.96	
27	2.83	3.12	3.29	3.41	3.50	3.57	3.63	3.68	3.73	3.77	3.81	3.84	3.87	3.90	3.93	
28	2.82	3.11	3.27	3.39	3.48	3.55	3.61	3.66	3.71	3.75	3.79	3.82	3.85	3.88	3.91	
29	2.81	3.10	3.26	3.38	3.46	3.54	3.60	3.65	3.69	3.73	3.77	3.80	3.83	3.86	3.89	
30	2.80	3.09	3.25	3.36	3.45	3.52	3.58	3.63	3.68	3.72	3.76	3.79	3.82	3.85	3.87	
31	2.79	3.08	3.24	3.35	3.44	3.51	3.57	3.62	3.66	3.70	3.74	3.77	3.80	3.83	3.85	
32	2.78	3.07	3.23	3.34	3.43	3.50	3.56	3.60	3.65	3.69	3.73	3.76	3.79	3.81	3.84	
33	2.78	3.06	3.22	3.33	3.41	3.49	3.54	3.59	3.64	3.67	3.71	3.74	3.77	3.80	3.82	
34	2.77	3.05	3.21	3.32	3.40	3.47	3.53	3.58	3.62	3.66	3.70	3.73	3.76	3.78	3.81	
35	2.77	3.04	3.20	3.31	3.39	3.46	3.52	3.57	3.61	3.65	3.69	3.72	3.75	3.77	3.80	
36	2.76	3.04	3.19	3.30	3.39	3.45	3.51	3.56	3.60	3.64	3.67	3.71	3.73	3.76	3.79	
37	2.76	3.03	3.19	3.29	3.38	3.44	3.50	3.55	3.59	3.63	3.66	3.69	3.72	3.75	3.77	
38	2.75	3.02	3.18	3.29	3.37	3.44	3.49	3.54	3.58	3.62	3.65	3.68	3.71	3.74	3.76	
39	2.75	3.02	3.17	3.28	3.36	3.43	3.48	3.53	3.57	3.61	3.64	3.67	3.70	3.73	3.75	
40	2.74	3.01	3.17	3.27	3.35	3.42	3.47	3.52	3.56	3.60	3.63	3.67	3.69	3.72	3.74	
41	2.74	3.01	3.16	3.27	3.35	3.41	3.47	3.51	3.56	3.59	3.63	3.66	3.68	3.71	3.73	
42	2.73	3.00	3.16	3.26	3.34	3.41	3.46	3.51	3.55	3.59	3.62	3.65	3.68	3.70	3.73	
43	2.73	3.00	3.15	3.25	3.33	3.40	3.45	3.50	3.54	3.58	3.61	3.64	3.67	3.69	3.72	
44	2.73	2.99	3.14	3.25	3.33	3.39	3.45	3.49	3.54	3.57	3.60	3.63	3.66	3.69	3.71	
45	2.73	2.99	3.14	3.24	3.32	3.39	3.44	3.49	3.53	3.56	3.60	3.63	3.65	3.68	3.70	
46	2.72	2.98	3.13	3.24	3.32	3.38	3.43	3.48	3.52	3.56	3.59	3.62	3.65	3.67	3.70	
47	2.72	2.98	3.13	3.23	3.31	3.38	3.43	3.48	3.52	3.55	3.58	3.61	3.64	3.67	3.69	
48	2.71	2.98	3.12	3.23	3.31	3.37	3.42	3.47	3.51	3.55	3.58	3.61	3.63	3.66	3.68	
49	2.71	2.97	3.12	3.22	3.30	3.37	3.42	3.46	3.50	3.54	3.57	3.60	3.63	3.65	3.68	
50	2.71	2.97	3.12	3.22	3.30	3.36	3.41	3.46	3.50	3.53	3.57	3.60	3.62	3.65	3.67	
60	2.68	2.94	3.08	3.18	3.26	3.32	3.37	3.42	3.46	3.49	3.53	3.55	3.58	3.60	3.62	
70	2.67	2.92	3.06	3.16	3.24	3.30	3.35	3.39	3.43	3.46	3.49	3.52	3.54	3.57	3.59	
80	2.66	2.91	3.05	3.14	3.22	3.28	3.33	3.37	3.41	3.44	3.47	3.50	3.52	3.54	3.57	
90	2.65	2.89	3.03	3.13	3.20	3.26	3.31	3.35	3.39	3.42	3.45	3.48	3.50	3.53	3.55	
100	2.64	2.89	3.02	3.12	3.19	3.25	3.30	3.34	3.38	3.41	3.44	3.46	3.49	3.51	3.53	

Factor = $t_{(n-1,1-\alpha/2k)}\sqrt{1+1/n}$

transformation appears to be a natural choice for better approximating the assumed normality of the statistical procedure. Indeed, the transformation appears to have somewhat normalized the distribution of these measurements.

Assuming that we are interested in evaluating a single new downgradient measurement, the 99% prediction limit based on the original data is:

$$27.00 + 20.97(3.16) = 93.27 \text{ ppb}$$

whereas, the 99% prediction limit for the log transformed data is:

$$\exp[2.96 + .95(3.16)] = 388.39 \text{ ppb}$$

Alternatively, if we directly estimate the mean and standard deviation of the lognormal distribution (Aitchison, 1955), we obtain for the 99% prediction limit

$$28.16 + 27.71(3.16) = 115.73 \text{ ppb}$$

Inspection of these three prediction limits reveals that the estimate based on log transformed data is remarkably elevated relative to the normal and lognormal interval estimates. The lognormal prediction limit is, of course, incorrect because the use of these limits assumes a normal distribution for x, whereas these estimates are based on log-

purposes. Conversely, the interval estimate obtained following log transformation of the data, a seemingly standard and benign practice, is extremely high and is likely to lead to elevated false negative rates even for liberal effect magnitudes. In fact, the limit value for the log transformed data is almost an entire order of magnitude higher than the maximum value in the background sample. It is for this reason that log transformation must be used very cautiously when constructing prediction intervals.

that both the original observations $(x_1, \ldots, x_n)$ and the future observations $(x_{n+1}, \ldots, x_{n+k})$ arise from the same probability distribution, namely, $N(\mu, \sigma^2)$. Since, in practice, μ and σ^2 are unknown quantities, we must estimate their value from a random sample of previous measurements by obtaining the sufficient statistics $\bar{x}$ and s, that is, the sample mean and standard deviation. If our background measurements consist of multiple quarterly measurements of a single well or multiple upgradient wells at a single time-point,

Table 5. Factors for Obtaining Two-Sided 99% Prediction Limits for k Additional Samples Given a Background Sample of Size n

Previous	Number of new measurements (k)														
n	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
4	11.74	11.90	12.05	12.20	12.34	12.47	12.60	12.72	12.84	12.96	13.08	13.19	13.29	13.39	13.49
5	8.85	8.96	9.06	9.16	9.25	9.34	9.43	9.50	9.58	9.65	9.73	9.80	9.86	9.93	9.99
6	7.59	7.67	7.74	7.81	7.88	7.75	7.81	7.87	7.93	7.99	8.04	8.09	8.14	8.19	8.24
7	6.82	6.88	6.94	6.99	6.75	6.81	6.86	6.91	6.96	7.00	7.04	7.09	7.13	7.17	7.20
8	6.06	6.00	6.05	6.10	6.15	6.20	6.24	6.28	6.32	6.36	6.40	6.43	6.47	6.50	6.53
9	5.55	5.60	5.64	5.69	5.73	5.77	5.81	5.84	5.88	5.91	5.94	5.97	6.00	6.03	6.06
10	5.26	5.30	5.34	5.38	5.42	5.45	5.49	5.52	5.55	5.58	5.61	5.64	5.66	5.69	5.72
11	5.05	5.07	5.11	5.15	5.18	5.21	5.24	5.27	5.30	5.33	5.36	5.38	5.41	5.43	5.45
12	4.86	4.89	4.93	4.96	4.99	5.02	5.05	5.08	5.11	5.13	5.16	5.18	5.20	5.22	5.25
13	4.71	4.75	4.78	4.81	4.84	4.87	4.90	4.92	4.95	4.97	5.00	5.02	5.04	5.06	5.08
14	4.60	4.63	4.66	4.69	4.72	4.75	4.77	4.80	4.82	4.84	4.86	4.88	4.90	4.92	4.94
15	4.50	4.53	4.56	4.59	4.61	4.64	4.66	4.69	4.71	4.73	4.75	4.77	4.79	4.81	4.83
16	4.41	4.45	4.47	4.50	4.53	4.55	4.57	4.60	4.62	4.64	4.66	4.68	4.70	4.71	4.73
17	4.34	4.37	4.40	4.43	4.45	4.47	4.50	4.52	4.54	4.56	4.58	4.60	4.61	4.63	4.65
18	4.28	4.31	4.34	4.36	4.39	4.41	4.43	4.45	4.47	4.49	4.51	4.53	4.54	4.56	4.58
19	4.23	4.25	4.28	4.31	4.33	4.35	4.37	4.39	4.41	4.43	4.45	4.47	4.48	4.50	4.51
20	4.18	4.21	4.23	4.26	4.28	4.30	4.32	4.34	4.36	4.38	4.39	4.41	4.43	4.44	4.46
21	4.14	4.16	4.19	4.21	4.23	4.25	4.27	4.29	4.31	4.33	4.35	4.36	4.38	4.39	4.41
22	4.10	4.13	4.15	4.17	4.19	4.21	4.23	4.25	4.27	4.29	4.30	4.32	4.34	4.35	4.36
23	4.06	4.09	4.11	4.14	4.16	4.18	4.20	4.21	4.23	4.25	4.27	4.28	4.30	4.31	4.32
24	4.03	4.06	4.08	4.10	4.13	4.14	4.16	4.18	4.20	4.21	4.23	4.25	4.26	4.28	4.29
25	4.00	4.03	4.05	4.07	4.09	4.11	4.13	4.15	4.17	4.18	4.20	4.21	4.23	4.24	4.26
26	3.98	4.00	4.03	4.05	4.07	4.09	4.10	4.12	4.14	4.16	4.17	4.19	4.20	4.21	4.23
27	3.96	3.98	4.00	4.02	4.04	4.06	4.08	4.10	4.11	4.13	4.14	4.16	4.17	4.19	4.20
28	3.93	3.96	3.98	4.00	4.02	4.04	4.05	4.07	4.09	4.11	4.12	4.13	4.15	4.16	4.17
29	3.91	3.94	3.96	3.98	4.00	4.02	4.03	4.05	4.07	4.08	4.10	4.11	4.13	4.14	4.15
30	3.90	3.92	3.94	3.96	3.98	4.00	4.01	4.03	4.05	4.06	4.08	4.09	4.10	4.12	4.13
31	3.88	3.90	3.92	3.94	3.96	3.98	4.00	4.01	4.03	4.04	4.06	4.07	4.09	4.10	4.11
32	3.86	3.88	3.91	3.93	3.94	3.96	3.98	4.00	4.01	4.03	4.04	4.06	4.07	4.08	4.09
33	3.85	3.87	3.89	3.91	3.93	3.95	3.96	3.98	3.99	4.01	4.02	4.04	4.05	4.06	4.08
34	3.83	3.86	3.88	3.90	3.91	3.93	3.95	3.96	3.98	3.99	4.01	4.02	4.03	4.05	4.06
35	3.82	3.84	3.86	3.88	3.90	3.92	3.93	3.95	3.97	3.98	3.99	4.01	4.02	4.03	4.04
36	3.81	3.83	3.85	3.87	3.89	3.90	3.92	3.94	3.95	3.97	3.98	3.99	4.01	4.02	4.03
37	3.80	3.82	3.84	3.86	3.88	3.89	3.91	3.92	3.94	3.95	3.97	3.98	3.99	4.01	4.02
38	3.79	3.81	3.83	3.85	3.86	3.88	3.90	3.91	3.93	3.94	3.95	3.97	3.98	3.99	4.00
39	3.78	3.80	3.82	3.84	3.85	3.87	3.89	3.90	3.92	3.93	3.94	3.96	3.97	3.98	3.99
40	3.77	3.79	3.81	3.83	3.84	3.86	3.88	3.89	3.91	3.92	3.93	3.95	3.96	3.97	3.98
41	3.76	3.78	3.80	3.82	3.83	3.85	3.87	3.88	3.90	3.91	3.92	3.94	3.95	3.96	3.97
42	3.75	3.77	3.79	3.81	3.82	3.84	3.86	3.87	3.89	3.90	3.91	3.93	3.94	3.95	3.96
43	3.74	3.76	3.78	3.80	3.82	3.83	3.85	3.86	3.88	3.89	3.90	3.92	3.93	3.94	3.95
44	3.73	3.75	3.77	3.79	3.81	3.82	3.84	3.85	3.87	3.88	3.89	3.91	3.92	3.93	3.94
45	3.72	3.74	3.76	3.78	3.80	3.81	3.83	3.85	3.86	3.87	3.89	3.90	3.91	3.92	3.93
46	3.72	3.74	3.76	3.77	3.79	3.81	3.82	3.84	3.85	3.87	3.88	3.89	3.90	3.91	3.93
47	3.71	3.73	3.75	3.77	3.78	3.80	3.82	3.83	3.84	3.86	3.87	3.88	3.90	3.91	3.92
48	3.70	3.72	3.74	3.76	3.78	3.79	3.81	3.82	3.84	3.85	3.86	3.88	3.89	3.90	3.91
49	3.70	3.72	3.74	3.75	3.77	3.79	3.80	3.82	3.83	3.84	3.86	3.87	3.88	3.89	3.90
50	3.69	3.71	3.73	3.75	3.76	3.78	3.80	3.81	3.82	3.84	3.85	3.86	3.87	3.89	3.90
60	3.64	3.66	3.68	3.70	3.71	3.73	3.74	3.76	3.77	3.78	3.80	3.81	3.82	3.83	3.84
70	3.61	3.63	3.65	3.66	3.68	3.69	3.71	3.72	3.74	3.75	3.76	3.77	3.78	3.79	3.80
80	3.59	3.60	3.62	3.64	3.65	3.67	3.68	3.70	3.71	3.72	3.73	3.74	3.75	3.76	3.78
90	3.57	3.58	3.60	3.62	3.63	3.65	3.66	3.67	3.69	3.70	3.71	3.72	3.73	3.74	3.75
100	3.55	3.57	3.59	3.60	3.62	3.63	3.65	3.66	3.67	3.68	3.69	3.71	3.72	3.73	3.74

Factor $= t_{n-1,.995}\sqrt{1 + 1/n}$

Previous n	Number of new measurements (k)														
	30	[illegible]	40	45	50	55	60	65	70	75	80	85	90	95	100
4	13.47	13.[illegible]	14.31	14.84	14.98	15.37	15.54	15.80	16.26	16.28	16.45	16.86	16.86	17.25	17.30
5	9.99	10.20	10.54	10.77	10.98	11.17	11.36	11.51	11.67	11.81	11.94	12.07	12.19	12.31	12.43
6	8.34	8.48	8.66	8.83	8.97	9.11	9.24	9.36	9.48	9.58	9.68	9.77	9.86	9.95	10.03
7	7.30	7.38	7.53	7.67	7.79	7.90	8.01	8.10	8.19	8.28	8.35	8.43	8.50	8.57	8.63
8	6.53	6.68	6.81	6.92	7.02	7.13	7.20	7.29	7.36	7.43	7.50	7.56	7.62	7.67	7.72
9	6.06	6.19	6.30	6.40	6.49	6.57	6.65	6.72	6.78	6.84	6.90	6.96	7.00	7.05	7.10
10	5.72	5.83	5.93	6.02	6.10	6.17	6.24	6.30	6.36	6.41	6.46	6.51	6.56	6.60	6.64
11	5.45	5.56	5.65	5.73	5.80	5.87	5.93	5.99	6.04	6.09	6.13	6.18	6.22	6.25	6.29
12	5.25	5.34	5.43	5.50	5.57	5.63	5.69	5.74	5.79	5.83	5.87	5.91	5.95	5.98	6.02
13	5.08	5.17	5.26	5.32	5.38	5.44	5.49	5.54	5.58	5.62	5.66	5.70	5.74	5.77	5.80
14	4.94	5.03	5.10	5.17	5.23	5.28	5.33	5.38	5.42	5.46	5.49	5.53	5.56	5.59	5.62
15	4.82	4.91	4.98	5.04	5.10	5.15	5.20	5.24	5.28	5.32	5.35	5.38	5.42	5.45	5.47
16	4.73	4.81	4.88	4.94	4.99	5.04	5.08	5.13	5.16	5.20	5.23	5.26	5.29	5.32	5.35
17	4.65	4.72	4.79	4.85	4.90	4.94	4.98	5.03	5.06	5.10	5.13	5.16	5.19	5.21	5.24
18	4.58	4.65	4.71	4.77	4.82	4.86	4.90	4.94	4.98	5.01	5.04	5.07	5.10	5.12	5.15
19	4.51	4.58	4.64	4.70	4.75	4.79	4.83	4.87	4.90	4.93	4.96	4.99	5.02	5.04	5.06
20	4.46	4.53	4.59	4.64	4.68	4.73	4.77	4.80	4.83	4.86	4.89	4.92	4.95	4.97	4.99
21	4.41	4.48	4.53	4.58	4.63	4.67	4.71	4.74	4.77	4.80	4.83	4.86	4.88	4.91	4.93
22	4.36	4.43	4.49	4.54	4.58	4.62	4.66	4.69	4.72	4.75	4.78	4.80	4.83	4.85	4.87
23	4.32	4.39	4.44	4.49	4.54	4.58	4.61	4.64	4.67	4.70	4.73	4.75	4.78	4.80	4.82
24	4.28	4.35	4.41	4.45	4.50	4.53	4.57	4.60	4.63	4.66	4.69	4.71	4.73	4.76	4.78
25	4.26	4.32	4.37	4.42	4.46	4.50	4.53	4.56	4.59	4.62	4.65	4.67	4.69	4.71	4.73
26	4.23	4.29	4.34	4.39	4.43	4.46	4.50	4.53	4.56	4.58	4.61	4.63	4.66	4.68	4.70
27	4.20	4.26	4.31	4.36	4.40	4.43	4.47	4.50	4.53	4.55	4.58	4.60	4.62	4.64	4.66
28	4.17	4.23	4.28	4.33	4.37	4.40	4.44	4.47	4.50	4.52	4.55	4.57	4.59	4.61	4.63
29	4.15	4.21	4.26	4.30	4.34	4.38	4.41	4.44	4.47	4.49	4.52	4.54	4.56	4.58	4.60
30	4.13	4.19	4.24	4.28	4.32	4.35	4.39	4.42	4.44	4.47	4.49	4.51	4.53	4.55	4.57
31	4.11	4.17	4.22	4.26	4.30	4.33	4.36	4.39	4.42	4.44	4.47	4.49	4.51	4.53	4.55
32	4.09	4.15	4.20	4.24	4.28	4.31	4.34	4.37	4.40	4.42	4.45	4.47	4.49	4.51	4.53
33	4.08	4.13	4.18	4.22	4.26	4.29	4.32	4.35	4.38	4.40	4.42	4.45	4.47	4.49	4.51
34	4.06	4.11	4.16	4.20	4.24	4.27	4.30	4.33	4.36	4.38	4.40	4.43	4.45	4.47	4.48
35	4.04	4.10	4.15	4.19	4.22	4.26	4.28	4.31	4.34	4.36	4.39	4.41	4.43	4.45	4.46
36	4.03	4.08	4.13	4.17	4.21	4.24	4.27	4.30	4.32	4.35	4.37	4.39	4.41	4.43	4.45
37	4.02	4.07	4.12	4.16	4.19	4.23	4.26	4.28	4.31	4.33	4.35	4.37	4.39	4.41	4.43
38	4.00	4.06	4.10	4.14	4.18	4.21	4.24	4.27	4.29	4.32	4.34	4.36	4.38	4.40	4.41
39	3.99	4.05	4.09	4.13	4.17	4.20	4.23	4.25	4.28	4.30	4.32	4.34	4.36	4.38	4.40
40	3.98	4.03	4.08	4.12	4.15	4.19	4.21	4.24	4.27	4.29	4.31	4.33	4.34	4.36	4.38
41	3.97	4.02	4.07	4.11	4.14	4.17	4.20	4.23	4.25	4.28	4.30	4.32	4.33	4.35	4.37
42	3.96	4.01	4.06	4.10	4.13	4.16	4.19	4.22	4.24	4.26	4.29	4.31	4.32	4.34	4.35
43	3.95	4.00	4.05	4.09	4.12	4.15	4.18	4.21	4.23	4.25	4.27	4.29	4.31	4.32	4.34
44	3.94	3.99	4.04	4.08	4.11	4.14	4.17	4.20	4.22	4.24	4.26	4.28	4.30	4.32	4.33
45	3.93	3.98	4.03	4.07	4.10	4.13	4.16	4.19	4.21	4.23	4.25	4.27	4.29	4.31	4.32
46	3.93	3.98	4.02	4.06	4.09	4.12	4.15	4.18	4.20	4.22	4.24	4.26	4.28	4.30	4.31
47	3.92	3.97	4.01	4.05	4.08	4.11	4.14	4.17	4.19	4.21	4.23	4.25	4.27	4.29	4.30
48	3.91	3.96	4.00	4.04	4.07	4.11	4.13	4.16	4.18	4.20	4.22	4.24	4.26	4.28	4.29
49	3.90	3.95	4.00	4.03	4.07	4.10	4.12	4.15	4.17	4.20	4.22	4.24	4.26	4.28	4.29
50	3.90	3.95	3.99	4.03	4.06	4.09	4.12	4.14	4.17	4.19	4.21	4.23	4.25	4.27	4.29
60	3.84	3.89	3.93	3.97	4.00	4.03	4.05	4.08	4.10	4.12	4.14	4.16	4.18	4.19	4.21
70	3.80	3.85	3.89	3.93	3.96	3.98	4.01	4.03	4.06	4.08	4.09	4.11	4.13	4.14	4.16
80	3.78	3.82	3.86	3.89	3.93	3.95	3.98	4.00	4.02	4.04	4.06	4.08	4.09	4.11	4.12
90	3.75	3.80	3.84	3.87	3.90	3.93	3.96	3.98	4.00	4.02	4.03	4.05	4.07	4.08	4.10
100	3.74	3.78	3.82	3.85	3.88	3.91	3.93	3.96	3.98	4.00	4.01	4.03	4.05	4.06	4.08

Factor = $t_{(n-1,1-\alpha/2k)}\sqrt{1+1/n}$

$s^2 = \sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)$ is an unbiased estimate of σ^2. However, when multiple upgradient wells are evaluated on several quarters, the previous equation yields biased results unless we make the demonstrably false assumption that temporal and spatial variability are identical.

The unbiased variance estimate for the case of multiple upgradient wells and multiple samplings of each well (selected at sufficient intervals to insure independence, for example, quarterly sampling) can be obtained from the *random effects* analysis of variance model [see Winer (1971), page 427, for a similar example]. Here, we are modeling the background measurements in terms of two random factors corresponding to wells and time-points. The general form of this model is given by:

$$x_{ij} = \mu + \omega_i + r_j + e_{ij}$$

where x_{ij} is the measurement on background (upgradient) well i on sampling event j; μ is the unknown mean level for background measurements (i.e., averaged across wells and time); ω_i is a random variable distributed $N(0, \sigma^2_\omega)$ that describes the

distributed $N(0, \sigma_\tau^2)$ that describes the deviation at time j from μ; and ϵ_{ij} is a random residual distributed $N(0, \sigma_\epsilon^2)$. Assuming independence of the x_{ij}, the expected value of a measurement is:

$$E(x_{ij}) = \mu$$

with variance

$$V(x_{ij}) = \sigma_\omega^2 + \sigma_\tau^2 + \sigma_\epsilon^2$$

This model corresponds to what is termed a *randomized block design* in the statistical literature, and the expected mean square for the wells, time-points, and residuals are given, respectively, as:

$$MS_\omega = t\sigma_\omega^2 + \sigma_\epsilon^2$$

$$= t \sum_{i=1}^{w} (\bar{x}_i - \bar{\bar{x}})^2/(w-1)$$

$$MS_\tau = w\sigma_\tau^2 + \sigma_\epsilon^2$$

$$= w \sum_{j=1}^{t} (\bar{x}_j - \bar{\bar{x}})^2/(t-1)$$

$$MS_\epsilon = \sigma_\epsilon^2$$

$$= \sum_{i=1}^{w} \sum_{j=1}^{t} (x_{ij} - \bar{x}_i - \bar{x}_j + \bar{\bar{x}})^2/(w-1)(t-1)$$

where x_{ij} is the measurement for well i on occasion j; w is the number of wells; t is the number of quarterly measurements per well; $\bar{x}_i$ is the mean for all measurements from well i; $\bar{x}_j$ is the mean for all measurements from time j; and $\bar{\bar{x}}$ is the mean of all measurements across wells and times.

Solving for the individual variance components σ_ω^2, σ_τ^2, and σ_ϵ^2, we find that:

$$\sigma_\omega^2 = \frac{MS_\omega - MS_\epsilon}{t}$$

$$\sigma_\tau^2 = \frac{MS_\tau - MS_\epsilon}{w}$$

and $$\sigma_\epsilon^2 = MS_\epsilon$$

The unbiased estimate of the total variance is therefore:

$$V(x_{ij}) = \sigma_\omega^2 + \sigma_\tau^2 + \sigma_\epsilon^2$$

$$= \frac{MS_\omega - MS_\epsilon}{t} + \frac{MS_\tau - MS_\epsilon}{w} + MS_\epsilon$$

The above model assumes that all wells are measured at the same time-points, and thus, the two factors are referred to as "crossed" factors. If the wells cannot be assumed to be equal, then the time point factor is said to be "nested" within the well factor [see Winer (1971), page 360, for a detailed description of nested factor designs]. This would occur, for instance, if the background observations for well 1 were made quarterly in 1972, while the observations for well 2 were made quarterly in 1976, and those for well 3 were made in 1975, etc. This nested model is given by:

$$x_{ij} = \mu + \omega_i + \tau_{ij} + \epsilon_{ij}$$

where x_{ij}, μ, ω_i, and ϵ_{ij} are as before, while τ_{ij} is a random variable distributed $N(0, \sigma_\tau^2)$ that describes the deviation of well i at time j from the overall mean value for well i ($\mu + \omega_i$) averaged over time.

If sampling events are "nested" within wells, the expected mean squares must be modified to reflect this design. Specifically, the expected mean square for the wells is:

$$MS_\omega = t\sigma_\omega^2 + \sigma_\tau^2 + \sigma_\epsilon^2$$

$$= t \sum_{i=1}^{w} (\bar{x}_i - \bar{\bar{x}})^2/(w-1)$$

while the mean square for time is:

$$MS_\tau = \sigma_\tau^2 + \sigma_\epsilon^2$$

$$= \sum_{i=1}^{w} \sum_{j=1}^{t} (x_{ij} - \bar{x}_i)^2/[w(t-1)]$$

With time nested within wells, the error term σ_ϵ^2 cannot be separately estimated since there is only one observation per well x time cell. Thus, solving for the individual variance components σ_ω^2 and σ_τ^2, we find that:

$$\sigma_\omega^2 = \frac{MS_\omega - MS_\tau}{t}$$

and $$\sigma_\tau^2 + \sigma_\epsilon^2 = MS_\tau$$

The unbiased estimate of the total variance is now:

$$V(x_{ij}) = \sigma_\omega^2 + \sigma_\tau^2 + \sigma_\epsilon^2$$

$$= \frac{MS_\omega - MS_\tau}{t} + MS_\tau$$

$$= \frac{t \sum_{i=1}^{w} \frac{(\bar{x}_i - \bar{\bar{x}})^2}{(w-1)} - \sum_{i=1}^{w} \sum_{j=1}^{t} \frac{(x_{ij} - \bar{\bar{x}})^2}{[w(t-1)]}}{t}$$

$$+ \sum_{i=1}^{w} \sum_{j=1}^{t} \frac{(x_{ij} - \bar{x}_i)^2}{[w(t-1)]}$$

variance estimate that assumes equal spatial and temporal variability as expectation (the author is grateful to an anonymous reviewer for raising this point):

$$E[s^2] = E\left[\sum_{i=1}^{w}\sum_{j=1}^{\ell}(x_{ij}-\bar{x}_i)^2/(n-1)\right]$$

$$= \frac{n-\ell}{n}\sigma_\omega^2 + \sigma_\tau^2 + \sigma_\epsilon^2$$

where n is the total number of measurements. This equation reveals that s^2 will always underestimate $V(x_{ij})$. For example, with two wells and four quarterly measurements, the contribution of the well variance σ_ω^2 is underestimated by 43%. The addition of two upgradient wells decreases this bias to 20%, and the addition of a second years background increases the bias only slightly to 23%.

When multiple upgradient wells comprise the background sample, the unbiased estimate $V(x_{ij})$ should *always* be used in place of s^2. The importance of using multiple upgradient wells is due both to the large spatial variability that is commonly observed for naturally occurring constituents of ground water and because it eliminates the confound between spatial variability and contamination. In the case of a single upgradient well, an upgradient versus downgradient difference may reflect either spatial variability or contamination (*i.e.*, there is no estimate of σ_ω^2). In contrast, when multiple upgradient wells are sampled, an estimate of spatial variability σ_ω^2 is available, and the resulting prediction limit will provide for spatial effects. A critical assumption, however, is that both spatial and temporal variability are the same for upgradient and downgradient locations. This is a complex problem, and the feasibility of this assumption should always be evaluated on a site-specific basis to bring into consideration hydrogeology as well as problems with previous conditions and sources of off-site contamination.

5. ILLUSTRATION

Consider the following data for pH obtained from two upgradient wells each with four quarterly measurements.

Quarter	Upgradient well 1	Upgradient well 2
1	7.1	7.7
2	7.4	7.8
3	7.7	7.9
4	8.0	8.0

$\bar{x}_{well1} = (7.1 + 7.4 + 7.7 + 8.0)/4 = 7.55$

$\bar{x}_{well2} = (7.7 + 7.8 + 7.9 + 8.0)/4 = 7.85$

$MS_\omega = 4[(7.55-7.70)^2 + (7.85-7.70)^2]/(2-1) = 0.180$

$MS_\tau = [(7.1-7.55)^2 + (7.4-7.55)^2 + (7.7-7.55)^2 + (8.0-7.55)^2 + (7.7-7.85)^2 + (7.8-7.85)^2 + (7.9-7.85)^2 + (8.0-7.85)^2]/[2(4-1)]$

$= 0.083$

The resulting variance estimates are therefore:

$$\sigma_\omega^2 = \frac{MS_\omega - MS_\tau}{\ell}$$

$$= (.180 - .083)/4 = 0.024$$

$$\sigma_\tau^2 = MS_\tau = 0.083$$

$$V(x_{ij}) = 0.108$$

As expected, the biased variance estimate $s^2 = .097$ underestimates $V(x_{ij})$ since, in this example, $s^2 = 4/7\sigma_\omega^2 + \sigma_\tau^2 + \sigma_\epsilon^2$. The variance estimate for the randomized blocks design $V(x_{ij}) = .120$ was somewhat larger than the result obtained for the nested model, because a unique estimate of the residual error is available ($\sigma_\omega^2 = .037$, $\sigma_\tau^2 = .050$, and $\sigma_\epsilon^2 = .033$).

In terms of establishing prediction intervals for future observations, we obtain the following estimates from Tables 4–6 assuming the more general nested sampling design (*i.e.*, the time-points are not the same for all wells).

Number of downgradient wells	Prediction interval		
1	$7.70 \pm 3.67(\sqrt{.108})$	=	6.49 - 8.91
2	$7.70 \pm 4.20(\sqrt{.108})$	=	6.32 - 9.08
3	$7.70 \pm 4.52(\sqrt{.108})$	=	6.22 - 9.19
4	$7.70 \pm 4.75(\sqrt{.108})$	=	6.13 - 9.26
5	$7.70 \pm 4.94(\sqrt{.108})$	=	6.08 - 9.32
6	$7.70 \pm 5.09(\sqrt{.108})$	=	6.03 - 9.37
7	$7.70 \pm 5.22(\sqrt{.108})$	=	5.98 - 9.42
8	$7.70 \pm 5.34(\sqrt{.108})$	=	5.94 - 9.46
9	$7.70 \pm 5.44(\sqrt{.108})$	=	5.91 - 9.49
10	$7.70 \pm 5.53(\sqrt{.108})$	=	5.88 - 9.52
20	$7.70 \pm 6.15(\sqrt{.108})$	=	5.68 - 9.72
30	$7.70 \pm 6.53(\sqrt{.108})$	=	5.55 - 9.85
40	$7.70 \pm 6.81(\sqrt{.108})$	=	5.46 - 9.94
50	$7.70 \pm 7.02(\sqrt{.108})$	=	5.39 - 10.01
100	$7.70 \pm 7.72(\sqrt{.108})$	=	5.16 - 10.24

one year), the prediction intervals would range from 6.70 to 8. for a single downgradient well to 5.94 to 9.46 for a site with 100 downgradient wells, assuming that $\bar{x}$ and $V(x_{ij})$ remained constant.

6. DISCUSSION

Although the statistical monitoring strategy developed here may appear comprehensive, it is only a small first step. For example, none of the methodology presented here is directly appropriate for the analysis of indicator compounds that exhibit values below method detection limits, or go undetected in a proportion of the sample. Perhaps, the simplest solution to this problem is to use the prediction limits developed here with estimates of the mean and variance of a censored normal distribution (Cohen, 1961) or censored lognormal distribution (Aitchison, 1955). Using these procedures, however, it is not at all clear how unbiased variance estimates would be obtained, as are described here for the case of complete information. As an even more extreme omission, the strategy presented here is completely inappropriate for the analysis of volatile organic compounds that occur in less than 5% of all measurements obtained from clean upgradient wells, trip blanks, and field blanks (Plumb and Parolini, 1986; Hurd, 1987). Inspections of these potentially useful indicator compounds suggest that they may arise from a Poisson process (Gibbons, 1987) or possibly even a censored Poisson distribution. Statistical methods for monitoring infrequently detected compounds, such as the volatile organic priority pollutant compounds are sorely needed in ground-water monitoring. and statistical research in this area is strongly encouraged.

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Statistical Models for the Analysis of Volatile Organic Compounds in Waste Disposal Sites

by Robert D. Gibbons

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Statistical Models for the Analysis of Volatile Organic Compounds in Waste Disposal Sites

by Robert D. Gibbons[a]

ABSTRACT

The occurrence of low-level hits of volatile organic priority pollutant compounds is statistically modeled as a Poisson process. Methods are developed to estimate the mean of the Poisson distribution for a random sample of volatile organic measurements as well as 99% prediction limits and 99% tolerance limits. The prediction limits provide an interval estimate that will include values obtained for the next k future measurements based on a sample of n previous measurements with 99% confidence. The tolerance limits provide an interval estimate for the n previous measurements that will contain 99% of the population of background measurements with 95% confidence. These methods are illustrated with measurements obtained from 61 field blanks, 56 trip blanks, and 162 samples obtained from 29 upgradient wells. Both prediction and tolerance limits yielded extremely similar results in all three examples.

1. INTRODUCTION

The current regulatory approach to ground-water monitoring at hazardous waste disposal facilities relies on "indicator parameters" to establish the need for more extensive characterization of ground-water monitoring samples. The critical assumption underlying this strategy is that the selected indicator parameters, pH, specific conductance (SC), total organic carbon (TOC), and total organic halogen (TOX), reflect levels of four major priority pollutant groups (volatiles, base/neutrals, acid extractables, and pesticides). If these four indicator parameters did serve as reasonable surrogates for the extensive list of priority pollutant compounds, statistical monitoring of these four compounds could indicate when analysis of the more extensive list was required. Based on a study of 350 CERCLA and RCRA sites and over 1000 elements and compounds, Plumb (1987) has demonstrated that increases in these four indicator parameters are rarely accompanied by increases in the levels of priority pollutant compounds. In fact, the concordance rates were only 10% for TOC, 16% for TOX, 38% for pH, and 38% for SC. In contrast, use of the 32 volatile organic priority pollutant compounds (VOC) as indicator parameters produced a concordance rate of 80%, and the correlation between the number of detected VOCs and the total number of priority pollutant compounds detected was $r = .97$ (*i.e.*, VOCs accounted for 94% of the variation in the total number of priority pollutant compounds detected). In fact, 49 out of the top 50 detected contaminants were either VOCs or discrete pairs of VOCs (*e.g.*, benzene and chloroform detected in the same scan). This finding also holds for 97 out of the top 100 contaminants and 139 out of the top 150 contaminants. These results taken as a whole clearly indicate the superiority of VOCs as indicator parameters relative to the current use of pH, SC, TOC, and TOX.

Although VOCs may provide a major improvement over the previous indicator parameters, they are far more challenging from a statistical perspective. For example, Hurd (1987) has shown that low-level "hits" of VOCs are found in approximately 5% of trip blanks, field blanks, and clean upgradient

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field blanks, trip blanks, and clean upgradient wells exhibits virtually identic[illegible] patterns (see Table 1). Similarly, when compared to downgradient data, the same low-level hit distribution observed in blanks and upgradient data is found; however, in the case of downgradient wells a second elevated component distribution is also observed (see Table 1). This elevated component distribution presumably reflects those values obtained from contaminated wells. Simple inspection of Table 1 suggests that low-level "hits" are common in the 0-40 ppb range, whereas the contaminant distribution begins between 50 and 100 ppb.

What should be immediately obvious from Table 1 is that while VOCs are detected in background measurements, their frequency of detection classifies them as rare events. In light of this, it will take a considerable amount of monitoring to establish a site-specific background that is suitable for statistical predictions of limits for future downgradient measurements.

2. STATISTICAL PROCEDURES

2.1. Prediction Limits for a Normal Distribution

Inspection of the data in Table 1 suggests several statistical approaches. Perhaps the simplest procedure is to ignore the nondetected values and compute the mean and standard deviation of only those values that were, in fact, detected. Given the long right tail of the frequency distributions in Table 1, we might first transform the data by taking natural logarithms and compute the mean and standard deviation on a logarithmic scale. For example, the mean and standard deviation for the 123 detected field blanks is 2.78 ± 0.37, for the 76 detected trip blanks is 2.67 ± 0.47, and for the 393 detected values from the sample of 29 upgradient wells is 2.80 ± 0.38. Given these sample estimates, we may compute prediction limits (Hahn, 1969; Danlya and Guttman, 1982; Gibbons, 1987) that will contain all of the next k VOC measurements with 99% con[illegible]ence. In the present context, k represents the number of downgradient monitoring wells. For example, if we wished to obtain a limit value that would include the next single observation, assuming that we had estimated $\bar{y}_{log}$ and s_{log} from the sample of field blanks in Table 1, we would apply the equation:

$$\exp\{\bar{y}_{log} + \sqrt{1 + 1/n}\; t_{[n-1,\alpha]}\, s_{log}\}$$

which in this case would yield:

$$\exp\{2.78 + \sqrt{1 + 1/123}\; 2.37\,(0.37)\} = 38.88$$

or 39 ppb. Similarly, the 99% prediction limit based on trip blanks would be:

$$\exp\{2.67 + \sqrt{1 + 1/76}\; 2.38\,(0.47)\} = 44.52$$

or 45 ppb. Finally, the 99% prediction limit based on the 29 clean upgradient wells would be:

$$\exp\{2.80 + \sqrt{1 + 1/323}\; 2.33\,(0.38)\} = 39.92$$

or 40 ppb. These findings confirm what is evident from the frequency distributions in Table 1; namely, it is rare to find a VOC above 40 ppb in trip blanks, field blanks, or clean upgradient wells.

Statistically, there are two unattractive features of what has just been presented. First, in terms of our estimates for the sample of upgradient wells, the sample standard deviation is a biased estimate of the population parameter σ, unless we assume that temporal and spatial variability are equivalent. Given that VOCs are not naturally occurring constituents of ground water, this may be a reasonable assumption; however, a more statistically rigorous approach would be to compute the total variance $V(x_{ij})$, where x_{ij} is the measurement on well i for monitoring event j using a *random effects* analysis of variance model (Winer, 1971, page 360). Details for obtaining unbiased estimates of σ in the context of ground-water monitoring are described by Gibbons (1987) and Starks (1986).

Second, it is difficult to justify simply ignoring those values that are not detected in computing estimates of μ and σ. Alternate procedures for estimating the mean and variance of a "censored" normal distribution (Cohen, 1961) or "censored" lognormal distribution (Aitchison, 1955) are available; however, these estimates are generally inappropriate for background samples in which only 5% of the data are actually detected. In the

Table 1. Frequency Distributions for Field Blanks, Trip Blanks, Clean Upgradient Wells, and Downgradient Wells

ppb	Field Blanks		Trip Blanks		Upgradient Wells		Downgradient Wells	
	n	%	n	%	n	%	n	%
ND	1965	(94%)	1777	(95%)	4981	(93%)	6023	(87%)
0-10	43	(2%)	42	(2.2%)	120	(2.4%)	296	(4.3%)
11-20	74	(3.5%)	28	(1.5%)	243	(4.5%)	330	(4.6%)
21-30	4	(0.2%)	2	(0.1%)	12	(0.2%)	30	(0.6%)
31-40	1	(0.05%)	3	(0.2%)	6	(0.1%)	28	(0.4%)
41-50	1	(0.05%)	0		1	(0.01%)	16	(0.2%)
51-100	0		1	(0.05%)	1	(0.01%)	49	(0.7%)
101-200	0		0		0		50	(0.9%)
200	0		0		0		93	(1.3%)
# of [illegible]	61		56		162		223	

[illegible]

following sectio model that incorporates both detected and nondetected values is presented.

2.2. The Poisson Distribution

In 1837 Poisson published the derivation of a distribution that bears his name. Poisson's approach was to derive a distribution for a series of independent events in which the number of trials were large, the probability of the occurrence of the outcome was small, and the probability remained constant over trials. In the classic illustration of the Poisson distribution, Bortkiewicz (1898) considered the number of deaths from being kicked by mules, per annum, in the Prussian Army Corps. In this case, the probability of death from this cause was small, and the number of soldiers exposed to risk was large. "Student" (W. S. Gosset) in 1907, used the Poisson distribution to represent the number of particles falling in a small area when a large number of areas are spread at random over a surface. Similarly, Rutherford and Geiger (1910) used the Poisson distribution to model variations in the number of particles emitted by a radioactive source per unit time.

In more recent years, the Poisson distribution has been used to characterize rare events such as suicide rates and the number of mutated cells on plates containing 10^4 cells.

In the context of ground-water monitoring, two applications of the Poisson distribution become evident. First, the number of "hits" out of a large number of VOC measurements could be modeled by the Poisson distribution (Silver and Dunn, 1986). Second, we might consider the molecule as a unit of observation and postulate that the number of molecules of a particular compound out of a much larger number of molecules of water is the result of a Poisson process. For example, we might consider 12 ppb of benzene to represent a count of 12 units of benzene for every billion units examined. In this context, Poisson's approach is justified in that the number of units (*i.e.*, molecules) examined is large, and the probability of the occurrence (*i.e.*, a molecule being classified as benzene) is small.

As an illustration of the Poisson distribution, consider the data for field blanks in Table 1. First, let us examine the question of, on the average, how many detected compounds can be expected to occur per scan of 32 compounds. The probability of a scan with exactly x detected compounds is:

$$f(x, \mu) = \frac{\mu^x}{x!} e^{-\mu}$$

where $x = 0, 1, 2, \ldots$, and $e = 2.718$. The term μ is the mean of the Poisson distribution; that is,

$$\mu = \sum_{x=0}^{\infty} x f(x)$$

for which the sample mean is the unbiased estimator; that is,

$$\hat{\mu} = \bar{x} = \sum_{i=1}^{N} x_i/n$$

For example, the probability of a sample with no detected compounds is:

$$f(0, \bar{x}) = e^{-\bar{x}}$$

and the probability of a sample with three detected compounds is:

$$f(3, \bar{x}) = \frac{\bar{x}^3 e^{-\bar{x}}}{(2)(3)}$$

The expected number of samples with three detected compounds is, therefore, $n f(3, \bar{x})$, where n is the number of samples.

Turning to our example of field blanks in Table 1, 123 detections are reported for 61 scans; therefore, $\bar{x} = 123/61$ or 2.02 detections per scan. The probability of a sample with five detected compounds is therefore:

$$f(5, 2.02) = \frac{(2.02)^5 e^{-2.02}}{5!} = 0.037$$

and we would expect 61(.037) = 2.26 out of 61 samples to have five detected compounds. Similarly, the probability of five detected compounds is $f(5, 1.36) = 0.01$ for trip blanks and $f(5, 2.42) = 0.06$ for the sample of 29 upgradient wells.

Although this example nicely illustrates the use of the Poisson distribution, it says nothing about the concentration of individual detected compounds. For example, four compounds detected at 10 ppb would provide exactly the same probability estimate as four compounds detected at 1 ppm!

Second, let us examine the case in which the molecule is the unit of observation. Returning to the field blank example, we find 2120 ppb out of a total of 61 samples; therefore, $\bar{x} = 2120/61$ or 34.75 ppb per sample. The probability of a sample with exactly 40 ppb is therefore:

$$f(40, 34.75) = \frac{(34.75)^{40} e^{-34.75}}{40!} = 0.04$$

One possible decision rule that can be generated from a Poisson distribution is to compute a limit value that will contain 99% of the previous background measurements with 95% confidence. Individual new downgradient sample values might then be informally compared to this tolerance limit. However, this comparison does not, in and of itself, constitute a statistical test of the null hypothesis that the new observation was drawn from the same distribution as the previous samples.

The uniformly most accurate upper tolerance limit for the Poisson distribution is given by Zacks (1970). The derivation begins by obtaining the cumulative probability that a or more occurrences will be observed:

$$P(a, \mu) = \sum_{x=a}^{\infty} f(x, \mu)$$

which can be computed as

$$P(a, \mu) = P(\chi^2[2a + 2] > 2\mu)$$

where $\chi^2[\gamma]$ designates a chi-square random variable with γ degrees of freedom. This relationship between the Poisson and chi-square distribution was first described by Hartley and Pearson (1950). Given n independent and identically distributed Poisson random variables (*i.e.*, one count per sample), the sum

$$T_n = \sum_{i=1}^{n} x_i$$

also has a Poisson distribution.

Substituting T_n for μ, we can find the value for which the cumulative probability is 99%; that is,

$$K_{.99}(T_n) = \frac{1}{2n} \chi^2_{.99}[2T_n + 2]$$

The 99% upper tolerance limit is therefore $P^{-1}[a; K_{.99}(T_n)]$ = least nonnegative integer j such that

$$\chi^2_{\alpha}[2j + 2] > 2K_{.99}(T_n)$$

where α is the required confidence level, say, 95%.

For example, in the previous field blank data set, we observed 123 detections out of 61 VOC scans; therefore, $T_n = 123$, and $n = 61$. The cumulative 99% probability point is [probability points of the chi-square distribution were obtained using the Peizer and Pratt approximation described by Maindonald (1984), page 294]

$$K_{.99}(123) = \frac{1}{122} \chi^2_{.99}[2(123) + 2] = \frac{302}{122} = 2.48$$

The 95% upper tolerance limit is obtained by finding the smallest nonnegative integer j such that:

$$\chi^2_{.05}[2j + 2] > 2(2.48)$$

Inspection of standard chi-square tables (extracted below for $j = 3$ to 6) reveals that the value of j that satisfies this equation is 5.

j	$\chi^2_{.05}[2j + 2]$
3	2.73
4	3.94
5	5.23
6	6.57

Therefore, the $P^{-1}[0.95; K_{.99}(123)]$ upper tolerance limit is five compounds per scan. For trip blanks $K_{.99}(76) = 1.76$; therefore, $j = 4 = \chi^2_{.05}[10] = 3.94 > 2(1.76)$, and the upper tolerance limit is four detected compounds per scan. Finally, for upgradient wells $K_{.99}(393) = 2.72$, and the upper tolerance limit is six compounds per scan; *i.e.*, $\chi^2_{.05}[2(6) + 2] = 6.57$, which is the smallest value of j that produces a chi-square value greater than $2(2.72) = 5.44$.

Turning to the second case in which the molecule is the unit of observation, we obtain for field blanks,

$$K_{.99}(2120) = \frac{1}{122} \chi^2_{.99}[2(2120) + 2] = 36.52$$

and find that $j = 46$ satisfies the equation

$$\chi^2_{.05}[2(46) + 2] > 73.05$$

In this case, the value of j represents the total number of parts per billion detected in an entire volatile organic scan, that is, no more than 46 ppb per scan. The 99% tolerance limit for trip blanks was 32 ppb, and the upper 99% tolerance limit for the sample of 29 upgradient wells was 55 ppb.

2.4. Poisson Prediction Limits

The previously described tolerance limits provide interval estimates that contain a specified proportion of the population of background measurements with a certain level of confidence. A somewhat more appropriate interval estimate for the purpose of ground-water monitoring is a prediction limit which specifies an interval computed from n previous measurements that will contain k future measurements. In this context the

n previous measurements are either a series of site-specific scans, the trip blank and field blank measurements reported in Table 1, and the k future measurements refer to the observations obtained on the next monitoring event at k downgradient wells.

Cox and Hinkley (1974) consider the case in which y has a Poisson distribution with mean μ. Having observed y their goal is to predict y^* which has a Poisson distribution with mean $c\mu$ where c is a known constant. In the context of groundwater monitoring, y is the number of events observed in n previous samples, and y^* is the number of events observed in a single future sample; therefore, $c = 1/n$. Following Cox and Hinkley (1974) we develop a prediction limit using, as an approximation, the fact that the left side of:

$$\left(y^* - \frac{c(y+y^*)}{(1+c)}\right)^2 \Big/ \left(\frac{c(y+y^*)}{(1+c)^2}\right) < t^2_{[n-1,\alpha]}$$

is approximately a standard normal deviate; therefore, the $100(1-\alpha)\%$ prediction limit for y^* is formed from Student's t-distribution. Upon solving for y^* the upper limit value is found as the positive root of the quadratic equation:

$$y^* = \frac{2cy + t^2c + \sqrt{(-2cy - t^2c)^2 - 4[(cy)^2 - t^2cy]}}{2}$$

which after a bit of algebra simplifies somewhat to:

$$y^* = cy + \frac{t^2c}{2} + tc\sqrt{y(1+1/c) + t^2/4}$$

For example, applying this equation to the number of detected field blanks in Table 1 yields $y = 123$, $n = 61$, and $t_{[60,.01]} = 2.39$; therefore, the 99% upper prediction limit is:

$$y^* = \frac{123}{61} + \frac{(2.39)^2}{2(61)} + \frac{2.39}{61}\sqrt{123(1+61) + (2.39)^2/4}$$

$$= 5.47 \text{ detections per scan.}$$

When applied to the number of detected values for trip blanks, we have $y = 76$, $n = 56$, and $t_{[55,.01]} = 2.40$ which yields a 99% prediction limit of 3.23 detections per scan. Similarly, for upgradient wells, we have $y = 393$, $n = 162$, and $t_{[161,.01]} = 2.35$ which yields the 99% prediction limit for the next single measurement of 6.11 detections. These results are identical to the previously estimated tolerance limits which yielded [illegible] for field blanks, trip blanks, and upgradient wells, respectively.

Returning to the molecular approach, we may simply substitute previously defined values for y, such that we obtain for field blanks ($y = 2120$) a 99% upper prediction limit of 49 ppb per scan, for trip blanks ($y = 1260$) a 99% upper prediction limit of 34 ppb per scan, and for upgradient wells ($y = 6910$) a 99% upper prediction limit of 58 ppb per scan. Again, these prediction limit values are extremely similar to their corresponding tolerance limit values of 46 ppb, 32 ppb, and 55 ppb, respectively.

The previous prediction limits can only be used to obtain a limit value that will include a single future measurement. A simple yet conservative approximate method for obtaining a limit value that will contain the next k future measurements, where k is the number of downgradient wells, can be obtained by substituting $t_{[n-1,\alpha/k]}$ for $t_{[n-1,\alpha]}$ in the previous equations. This method of obtaining prediction intervals is based on the Bonferroni inequality (Miller, 1966) and has been shown to be satisfactory for practical purposes in computing normal prediction limits by Hahn (1969). Tables 2-4 provide values of $t_{[n-1,\alpha/k]}$ for previous sample sizes of $n = 4$ to 100 and future samples of size 1 to 100, using the algorithm provided by Maindonald (1984).

The method developed for computing Poisson prediction limits is approximate due to the previously described normality assumption which leads to use of Student's t-distribution. These estimates should be adequate for practical purposes, and their similarity to the uniformly most accurate Poisson tolerance limits is strong support for this claim. Exact 99% prediction limits for the Poisson distribution do not appear to have been published in the statistical literature, although they may be obtained using Bayesian methods for interval estimation (Guttman, 1970). This derivation is beyond the scope of the present paper; however, work on this problem is currently under way.

3. SUMMARY

Volatile organic compounds are detected at low levels in trip blanks, field blanks, and clean upgradient wells. Inspection of the frequency distributions for these three sets of data clearly reveals the characteristic shape of a Poisson distribution. In contrast, similar data for a large sample of downgradient wells yields a much different frequency distribution which appears to be a mixture of two processes, one of low-level hit[illegible] similar to that observed in blanks and upgradient

Table 2. Values of t for Obtaining One-Sided 99% Prediction Limits for k Additional Samples Given a Background Sample of Si[illegible]

Previous n	Number of new measurements (k)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	4.54	5.84	6.63	7.31	7.80	8.21	8.51	8.76	8.97	9.15	9.30	9.43	9.55	9.65	9.75
5	3.75	4.60	5.21	5.67	6.05	6.33	6.56	6.76	6.91	7.05	7.17	7.27	7.36	7.44	7.51
6	3.37	4.09	4.59	4.97	5.29	5.54	5.74	5.91	6.05	6.17	6.27	6.36	6.44	6.51	6.57
7	3.14	3.71	4.17	4.53	4.82	5.05	5.24	5.40	5.51	5.64	5.73	5.81	5.89	5.95	6.01
8	2.98	3.50	3.95	4.28	4.56	4.78	4.96	5.11	5.24	5.35	5.45	5.53	5.60	5.67	5.73
9	2.90	3.36	3.79	4.11	4.38	4.59	4.77	4.91	5.04	5.15	5.24	5.32	5.39	5.45	5.51
10	2.82	3.25	3.68	3.99	4.25	4.46	4.62	4.77	4.89	4.99	5.08	5.16	5.23	5.29	5.34
11	2.76	3.17	3.59	3.89	4.14	4.35	4.51	4.65	4.77	4.87	4.96	5.03	5.10	5.16	5.21
12	2.71	3.10	3.51	3.80	4.05	4.25	4.41	4.55	4.67	4.76	4.85	4.92	4.99	5.05	5.10
13	2.68	3.05	3.46	3.75	3.99	4.19	4.35	4.48	4.60	4.69	4.77	4.85	4.91	4.97	5.02
14	2.65	3.01	3.41	3.70	3.94	4.13	4.29	4.42	4.53	4.63	4.71	4.78	4.85	4.90	4.95
15	2.62	2.97	3.37	3.65	3.89	4.08	4.24	4.37	4.48	4.57	4.65	4.72	4.79	4.84	4.89
16	2.60	2.94	3.34	3.62	3.86	4.04	4.20	4.33	4.44	4.53	4.61	4.68	4.74	4.80	4.85
17	2.58	2.92	3.31	3.59	3.83	4.01	4.17	4.29	4.40	4.49	4.57	4.64	4.70	4.76	4.81
18	2.57	2.90	3.28	3.57	3.81	3.98	4.14	4.26	4.37	4.46	4.54	4.61	4.67	4.73	4.78
19	2.55	2.88	3.26	3.54	3.78	3.96	4.11	4.24	4.34	4.43	4.51	4.58	4.64	4.70	4.75
20	2.54	2.86	3.24	3.52	3.76	3.93	4.09	4.21	4.32	4.41	4.48	4.55	4.62	4.67	4.72
21	2.53	2.84	3.22	3.50	3.74	3.91	4.07	4.19	4.30	4.38	4.46	4.53	4.59	4.65	4.70
22	2.52	2.83	3.21	3.48	3.72	3.89	4.05	4.17	4.28	4.36	4.44	4.51	4.57	4.63	4.68
23	2.51	2.82	3.19	3.47	3.71	3.88	4.03	4.16	4.26	4.35	4.42	4.49	4.55	4.61	4.66
24	2.50	2.81	3.18	3.46	3.70	3.87	4.02	4.14	4.25	4.33	4.41	4.47	4.54	4.59	4.65
25	2.49	2.80	3.17	3.45	3.68	3.86	4.01	4.13	4.23	4.32	4.39	4.46	4.52	4.58	4.63
26	2.48	2.79	3.16	3.44	3.67	3.84	3.99	4.12	4.22	4.31	4.38	4.45	4.51	4.57	4.62
27	2.48	2.78	3.15	3.43	3.66	3.83	3.98	4.11	4.21	4.30	4.37	4.44	4.50	4.56	4.61
28	2.47	2.77	3.14	3.42	3.65	3.82	3.97	4.10	4.20	4.29	4.36	4.43	4.49	4.55	4.59
29	2.47	2.76	3.13	3.41	3.64	3.81	3.96	4.09	4.19	4.28	4.35	4.42	4.48	4.54	4.58
30	2.46	2.76	3.13	3.41	3.63	3.80	3.96	4.08	4.18	4.27	4.34	4.41	4.47	4.53	4.58
31	2.46	2.75	3.12	3.40	3.63	3.80	3.95	4.08	4.17	4.26	4.33	4.40	4.46	4.52	4.57
32	2.45	2.74	3.11	3.39	3.62	3.79	3.94	4.07	4.17	4.25	4.33	4.39	4.45	4.51	4.56
33	2.45	2.74	3.10	3.39	3.61	3.78	3.94	4.06	4.16	4.25	4.32	4.39	4.45	4.50	4.55
34	2.44	2.73	3.10	3.38	3.61	3.78	3.93	4.06	4.15	4.24	4.31	4.38	4.44	4.49	4.54
35	2.44	2.73	3.09	3.38	3.60	3.77	3.93	4.05	4.15	4.23	4.31	4.37	4.43	4.48	4.53
36	2.44	2.72	3.08	3.37	3.60	3.77	3.92	4.05	4.14	4.23	4.30	4.37	4.43	4.47	4.52
37	2.43	2.72	3.08	3.36	3.59	3.76	3.91	4.04	4.14	4.22	4.30	4.36	4.42	4.47	4.51
38	2.43	2.72	3.07	3.36	3.59	3.76	3.91	4.04	4.13	4.22	4.29	4.36	4.42	4.46	4.51
39	2.43	2.71	3.07	3.36	3.58	3.75	3.91	4.03	4.13	4.21	4.29	4.35	4.41	4.46	4.50
40	2.43	2.71	3.07	3.35	3.58	3.75	3.90	4.03	4.12	4.21	4.28	4.35	4.41	4.45	4.50
41	2.42	2.70	3.06	3.35	3.58	3.75	3.90	4.02	4.12	4.20	4.28	4.34	4.40	4.45	4.49
42	2.42	2.70	3.06	3.35	3.57	3.74	3.89	4.02	4.11	4.20	4.27	4.34	4.40	4.44	4.49
43	2.42	2.70	3.05	3.34	3.57	3.74	3.89	4.01	4.11	4.19	4.27	4.33	4.39	4.44	4.48
44	2.42	2.69	3.05	3.34	3.57	3.73	3.88	4.01	4.10	4.19	4.26	4.33	4.39	4.43	4.48
45	2.41	2.69	3.05	3.34	3.56	3.73	3.88	4.00	4.10	4.18	4.26	4.32	4.38	4.43	4.47
46	2.41	2.69	3.04	3.33	3.56	3.73	3.87	4.00	4.09	4.18	4.25	4.32	4.38	4.42	4.47
47	2.41	2.69	3.04	3.33	3.56	3.72	3.87	4.00	4.09	4.17	4.25	4.31	4.37	4.42	4.46
48	2.41	2.68	3.04	3.33	3.55	3.72	3.87	3.99	4.09	4.17	4.24	4.31	4.37	4.41	4.46
49	2.41	2.68	3.04	3.33	3.55	3.72	3.86	3.99	4.08	4.17	4.24	4.31	4.36	4.41	4.45
50	2.40	2.68	3.03	3.32	3.55	3.72	3.86	3.99	4.08	4.16	4.24	4.30	4.36	4.41	4.45
60	2.39	2.66	3.01	3.30	3.53	3.69	3.84	3.97	4.06	4.14	4.21	4.28	4.33	4.38	4.42
70	2.38	2.65	2.99	3.28	3.51	3.67	3.82	3.95	4.04	4.12	4.19	4.26	4.31	4.36	4.40
80	2.37	2.64	2.98	3.27	3.49	3.66	3.81	3.94	4.03	4.11	4.18	4.24	4.30	4.35	4.39
90	2.37	2.63	2.97	3.26	3.48	3.65	3.80	3.93	4.02	4.10	4.17	4.23	4.29	4.34	4.38
100	2.36	2.63	2.97	3.25	3.48	3.64	3.79	3.92	4.01	4.09	4.16	4.23	4.28	4.33	4.38

Factor = $t_{(n-1,1-\alpha/k)}$

wells, and a second elevated component distribution that probably represents contamination.

In this paper, interval estimates have been derived which (a) contain a specified proportion of the background measurements with a given level of confidence (*i.e.*, a tolerance limit), and (b) allow us to predict the maximum allowable value of a series of future measurements obtained from one or more downgradient wells, based on the results of a [illegible] measurements (*i.e.*, a prediction limit).

These interval estimates have been constructed both for the absolute number of detected compounds and for their concentration, which is measured in terms of the total number of detected parts per billion per volatile organic scan.

Application of these estimates to actual volatile organic data sets revealed remarkably consistent results. In the sample of field blanks, we find that no more than five detected compounds in a single scan are permissible, and that the number

of detected parts per billion for the entire scan cannot exceed 49 ppb. In terms of trip blanks, the results are somewhat lower (*i.e.*, four compounds and 34 ppb detected per scan) and slightly higher for upgradient wells (*i.e.*, six compounds detected per scan at no more than a total of 58 ppb). Interestingly, if we had simply computed normal prediction limits on only those measurements that were detected, we would have obtained 99% upper limit values around 40 ppb for all three sets.

In addition to the methods outlined here, alternative strategies are also available. As previously mentioned, exact 99% prediction intervals could be developed using Bayesian methods. Work in this area is currently under w Alternatively, we might consider estimates base on a censored Poisson distribution (Cohen, 195

Table 3. Values of t for Obtaining One-Sided 99% Prediction Limits for k Additional Samples Given a Background Sample of Size n

Previous n	Number of new measurements (k)														
	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
4	8.96	9.01	9.21	9.33	9.44	9.54	9.65	9.75	9.84	9.93	10.02	10.11	10.19	10.27	10.35
5	7.05	7.11	7.20	7.28	7.36	7.43	7.50	7.57	7.63	7.70	7.76	7.82	7.87	7.93	7.98
6	6.03	6.10	6.16	6.22	6.28	6.34	6.39	6.44	6.49	6.54	6.59	6.63	6.68	6.72	6.76
7	5.43	5.48	5.54	5.59	5.64	5.68	5.73	5.77	5.81	5.85	5.89	5.93	5.96	6.00	6.03
8	5.03	5.08	5.13	5.17	5.21	5.25	5.29	5.33	5.37	5.40	5.43	5.46	5.49	5.52	5.55
9	4.75	4.80	4.84	4.88	4.92	4.96	4.99	5.03	5.06	5.09	5.11	5.14	5.16	5.19	5.22
10	4.55	4.59	4.63	4.66	4.69	4.73	4.76	4.79	4.82	4.84	4.87	4.90	4.92	4.94	4.97
11	4.39	4.42	4.46	4.49	4.53	4.56	4.58	4.61	4.64	4.66	4.69	4.71	4.73	4.75	4.78
12	4.26	4.30	4.33	4.36	4.39	4.42	4.45	4.47	4.50	4.53	4.54	4.57	4.59	4.61	4.63
13	4.16	4.19	4.23	4.25	4.28	4.31	4.34	4.36	4.38	4.41	4.43	4.45	4.47	4.49	4.51
14	4.08	4.11	4.14	4.17	4.19	4.22	4.24	4.27	4.29	4.31	4.33	4.35	4.37	4.39	4.41
15	4.01	4.04	4.07	4.09	4.12	4.14	4.17	4.19	4.21	4.23	4.25	4.27	4.29	4.31	4.33
16	3.95	3.98	4.00	4.03	4.05	4.08	4.10	4.12	4.14	4.16	4.18	4.20	4.22	4.24	4.25
17	3.90	3.93	3.96	3.98	4.00	4.03	4.05	4.07	4.09	4.11	4.13	4.14	4.16	4.17	4.19
18	3.86	3.89	3.91	3.93	3.95	3.98	4.00	4.02	4.04	4.05	4.07	4.09	4.11	4.13	4.14
19	3.81	3.84	3.86	3.89	3.91	3.93	3.95	3.97	3.99	4.01	4.03	4.04	4.06	4.08	4.09
20	3.78	3.80	3.83	3.85	3.88	3.90	3.92	3.94	3.96	3.97	3.99	4.00	4.02	4.04	4.05
21	3.75	3.77	3.80	3.82	3.84	3.86	3.88	3.90	3.91	3.93	3.95	3.97	3.98	4.00	4.01
22	3.72	3.75	3.77	3.79	3.81	3.83	3.85	3.87	3.89	3.91	3.92	3.94	3.96	3.97	3.98
23	3.70	3.73	3.74	3.77	3.79	3.81	3.83	3.84	3.86	3.88	3.89	3.91	3.92	3.94	3.95
24	3.67	3.70	3.72	3.74	3.76	3.78	3.80	3.82	3.84	3.85	3.87	3.88	3.90	3.91	3.93
25	3.65	3.68	3.70	3.72	3.74	3.76	3.78	3.80	3.81	3.83	3.85	3.86	3.87	3.89	3.90
26	3.63	3.66	3.68	3.70	3.72	3.74	3.76	3.78	3.79	3.81	3.83	3.84	3.85	3.87	3.88
27	3.62	3.64	3.66	3.68	3.70	3.72	3.74	3.76	3.77	3.79	3.80	3.82	3.83	3.85	3.86
28	3.60	3.62	3.65	3.67	3.69	3.71	3.72	3.74	3.76	3.77	3.79	3.80	3.81	3.83	3.84
29	3.59	3.61	3.63	3.65	3.67	3.68	3.71	3.72	3.74	3.76	3.77	3.79	3.80	3.81	3.83
30	3.57	3.60	3.62	3.64	3.66	3.68	3.69	3.71	3.73	3.74	3.76	3.77	3.78	3.80	3.81
31	3.56	3.58	3.60	3.62	3.64	3.66	3.68	3.70	3.71	3.73	3.74	3.76	3.77	3.78	3.80
32	3.55	3.57	3.59	3.61	3.63	3.65	3.67	3.68	3.70	3.71	3.73	3.74	3.75	3.77	3.78
33	3.54	3.56	3.58	3.60	3.62	3.64	3.65	3.67	3.69	3.70	3.72	3.73	3.74	3.75	3.77
34	3.53	3.55	3.57	3.59	3.61	3.63	3.64	3.66	3.68	3.69	3.70	3.72	3.73	3.74	3.76
35	3.52	3.54	3.56	3.58	3.60	3.62	3.63	3.65	3.66	3.68	3.69	3.71	3.72	3.73	3.74
36	3.51	3.53	3.55	3.57	3.59	3.61	3.62	3.64	3.65	3.67	3.68	3.70	3.71	3.72	3.73
37	3.50	3.52	3.54	3.56	3.58	3.60	3.61	3.63	3.65	3.66	3.67	3.69	3.70	3.71	3.72
38	3.49	3.51	3.54	3.55	3.57	3.59	3.61	3.62	3.64	3.65	3.66	3.68	3.69	3.70	3.71
39	3.48	3.51	3.53	3.55	3.56	3.58	3.60	3.61	3.63	3.64	3.66	3.67	3.68	3.70	3.71
40	3.48	3.50	3.52	3.54	3.56	3.57	3.59	3.61	3.62	3.63	3.65	3.67	3.68	3.69	3.71
41	3.47	3.49	3.51	3.53	3.55	3.57	3.58	3.60	3.61	3.63	3.64	3.66	3.67	3.69	3.70
42	3.47	3.49	3.51	3.53	3.54	3.56	3.58	3.59	3.61	3.62	3.64	3.65	3.67	3.68	3.69
43	3.46	3.48	3.50	3.52	3.54	3.55	3.57	3.58	3.60	3.61	3.63	3.65	3.66	3.67	3.68
44	3.45	3.48	3.49	3.51	3.53	3.55	3.56	3.58	3.59	3.61	3.63	3.64	3.65	3.66	3.68
45	3.45	3.47	3.49	3.51	3.53	3.54	3.56	3.57	3.59	3.60	3.62	3.63	3.65	3.66	3.67
46	3.44	3.46	3.48	3.50	3.52	3.54	3.55	3.57	3.58	3.59	3.61	3.63	3.64	3.65	3.66
47	3.44	3.46	3.48	3.50	3.51	3.53	3.55	3.56	3.58	3.59	3.60	3.62	3.63	3.64	3.66
48	3.43	3.45	3.47	3.49	3.51	3.53	3.54	3.56	3.57	3.58	3.60	3.61	3.63	3.64	3.65
49	3.43	3.45	3.47	3.49	3.50	3.52	3.54	3.55	3.57	3.58	3.59	3.61	3.62	3.63	3.64
50	3.43	3.45	3.46	3.48	3.50	3.52	3.53	3.55	3.56	3.57	3.59	3.60	3.62	3.63	3.64
60	3.39	3.41	3.43	3.45	3.46	3.48	3.49	3.51	3.52	3.53	3.55	3.56	3.57	3.58	3.59
70	3.37	3.39	3.40	3.42	3.44	3.45	3.47	3.48	3.49	3.51	3.52	3.53	3.54	3.55	3.56
80	3.35	3.37	3.38	3.40	3.42	3.43	3.45	3.46	3.47	3.48	3.50	3.51	3.52	3.53	3.54
90	3.33	3.35	3.37	3.39	3.40	3.42	3.43	3.45	3.46	3.47	3.48	3.50	3.51	3.52	3.53
∞	3.27	3.29	3.30	3.32	3.33	3.35	3.36	3.37	3.38	3.39	3.40	3.41	3.42	3.43	3.44

Table 6. Values of t for Obtaining One Sided 99% Prediction Limits for k Additional Samples Given a Background Sample of Size n

Previous n	Number of new measurements (k)															
	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
4	10.35	10.71	11.00	11.23	11.43	11.59	11.74	11.87	11.98	12.08	12.17	12.25	12.32	12.39	12.45	12.50	12.55
5	7.98	8.23	8.44	8.61	8.76	8.89	9.00	9.10	9.19	9.27	9.34	9.41	9.47	9.52	9.57	9.62	9.66
6	6.79	6.96	7.11	7.24	7.35	7.44	7.53	7.61	7.68	7.74	7.80	7.86	7.91	7.96	8.00	8.04	8.08
7	6.03	6.19	6.32	6.44	6.55	6.64	6.74	6.82	6.90	6.96	7.02	7.08	7.13	7.17	7.22	7.26	7.29
8	5.55	5.69	5.80	5.90	6.00	6.08	6.16	6.23	6.30	6.36	6.42	6.47	6.52	6.57	6.62	6.66	6.70
9	5.22	5.35	5.45	5.55	5.61	5.68	5.75	5.81	5.87	5.93	5.98	6.03	6.07	6.12	6.16	6.20	6.24
10	4.97	5.07	5.17	5.25	5.32	5.39	5.45	5.51	5.56	5.61	5.65	5.70	5.74	5.78	5.82	5.86	5.89
11	4.78	4.87	4.96	5.03	5.10	5.16	5.22	5.27	5.32	5.37	5.41	5.45	5.49	5.53	5.56	5.60	5.63
12	4.63	4.72	4.80	4.87	4.93	4.99	5.04	5.09	5.13	5.17	5.21	5.26	5.29	5.33	5.35	5.39	5.42
13	4.51	4.59	4.67	4.73	4.79	4.85	4.89	4.94	4.98	5.02	5.06	5.09	5.13	5.16	5.19	5.22	5.25
14	4.41	4.49	4.56	4.62	4.68	4.73	4.77	4.82	4.86	4.89	4.93	4.96	4.99	5.02	5.05	5.08	5.11
15	4.32	4.40	4.47	4.53	4.58	4.63	4.67	4.72	4.75	4.79	4.82	4.86	4.88	4.91	4.94	4.97	4.99
16	4.25	4.33	4.39	4.45	4.50	4.55	4.59	4.63	4.67	4.70	4.73	4.76	4.79	4.82	4.84	4.87	4.89
17	4.19	4.26	4.33	4.38	4.43	4.48	4.52	4.55	4.59	4.62	4.65	4.68	4.71	4.74	4.76	4.78	4.81
18	4.14	4.21	4.27	4.32	4.37	4.41	4.45	4.49	4.52	4.56	4.59	4.61	4.64	4.66	4.69	4.71	4.73
19	4.09	4.16	4.22	4.27	4.32	4.36	4.40	4.43	4.47	4.50	4.53	4.55	4.58	4.60	4.63	4.65	4.67
20	4.05	4.12	4.17	4.23	4.27	4.31	4.35	4.38	4.42	4.45	4.47	4.50	4.53	4.55	4.57	4.60	4.62
21	4.01	4.08	4.14	4.19	4.23	4.27	4.31	4.34	4.37	4.40	4.43	4.45	4.48	4.50	4.53	4.55	4.57
22	3.98	4.05	4.10	4.15	4.19	4.23	4.27	4.30	4.33	4.36	4.39	4.41	4.44	4.46	4.48	4.50	4.52
23	3.96	4.02	4.07	4.12	4.16	4.20	4.23	4.27	4.30	4.33	4.36	4.39	4.41	4.44	4.46	4.48	4.50
24	3.93	3.99	4.04	4.09	4.13	4.17	4.20	4.23	4.26	4.29	4.32	4.35	4.37	4.40	4.42	4.44	4.46
25	3.90	3.96	4.01	4.06	4.10	4.14	4.17	4.21	4.23	4.26	4.29	4.32	4.34	4.36	4.38	4.41	4.43
26	3.88	3.94	3.99	4.04	4.08	4.11	4.15	4.18	4.21	4.23	4.26	4.29	4.31	4.33	4.35	4.37	4.39
27	3.86	3.92	3.97	4.01	4.05	4.09	4.12	4.15	4.18	4.21	4.23	4.26	4.28	4.30	4.32	4.34	4.36
28	3.84	3.90	3.95	3.99	4.03	4.07	4.10	4.13	4.16	4.19	4.21	4.23	4.26	4.28	4.30	4.32	4.34
29	3.82	3.88	3.93	3.98	4.01	4.05	4.08	4.11	4.14	4.16	4.19	4.21	4.23	4.25	4.27	4.29	4.31
30	3.81	3.87	3.91	3.96	4.00	4.03	4.06	4.09	4.12	4.14	4.17	4.19	4.21	4.23	4.25	4.27	4.29
31	3.79	3.85	3.90	3.94	3.98	4.01	4.05	4.07	4.10	4.13	4.15	4.17	4.19	4.21	4.23	4.25	4.27
32	3.78	3.84	3.88	3.93	3.96	4.00	4.03	4.05	4.08	4.11	4.13	4.15	4.17	4.19	4.21	4.23	4.25
33	3.77	3.82	3.87	3.91	3.95	3.98	4.01	4.04	4.07	4.09	4.12	4.14	4.16	4.18	4.20	4.22	4.24
34	3.76	3.81	3.86	3.90	3.94	3.97	4.00	4.03	4.05	4.08	4.10	4.12	4.14	4.16	4.18	4.20	4.22
35	3.74	3.80	3.85	3.89	3.92	3.96	3.99	4.02	4.04	4.06	4.09	4.11	4.13	4.15	4.17	4.19	4.21
36	3.73	3.79	3.83	3.88	3.91	3.95	3.98	4.00	4.03	4.05	4.07	4.09	4.11	4.13	4.15	4.17	4.19
37	3.72	3.78	3.82	3.86	3.90	3.93	3.96	3.99	4.01	4.04	4.06	4.08	4.10	4.12	4.14	4.16	4.18
38	3.71	3.77	3.81	3.85	3.89	3.92	3.95	3.98	4.00	4.03	4.05	4.07	4.09	4.11	4.13	4.15	4.17
39	3.71	3.76	3.80	3.84	3.88	3.91	3.94	3.97	3.99	4.02	4.04	4.06	4.08	4.10	4.12	4.14	4.16
40	3.70	3.75	3.80	3.84	3.87	3.90	3.93	3.96	3.98	4.01	4.03	4.05	4.07	4.09	4.11	4.13	4.15
41	3.69	3.74	3.79	3.83	3.86	3.89	3.92	3.95	3.97	4.00	4.02	4.04	4.06	4.08	4.10	4.11	4.13
42	3.68	3.73	3.78	3.82	3.85	3.89	3.91	3.94	3.97	3.99	4.01	4.03	4.05	4.07	4.09	4.10	4.12
43	3.68	3.73	3.77	3.81	3.85	3.88	3.91	3.93	3.96	3.98	4.00	4.02	4.04	4.06	4.08	4.09	4.11
44	3.67	3.72	3.76	3.80	3.84	3.87	3.90	3.92	3.95	3.97	3.99	4.01	4.03	4.05	4.07	4.08	4.10
45	3.66	3.71	3.76	3.80	3.83	3.86	3.89	3.92	3.94	3.96	3.98	4.00	4.02	4.04	4.06	4.07	4.09
46	3.66	3.71	3.75	3.79	3.82	3.86	3.88	3.91	3.93	3.96	3.98	4.00	4.02	4.04	4.05	4.07	4.08
47	3.65	3.70	3.74	3.78	3.82	3.85	3.88	3.90	3.93	3.95	3.97	3.99	4.01	4.03	4.05	4.06	4.08
48	3.64	3.70	3.74	3.78	3.81	3.84	3.87	3.90	3.92	3.94	3.96	3.98	4.00	4.02	4.04	4.05	4.07
49	3.64	3.69	3.73	3.77	3.81	3.84	3.86	3.89	3.91	3.94	3.96	3.98	4.00	4.02	4.03	4.05	4.07
50	3.63	3.68	3.73	3.77	3.80	3.83	3.86	3.88	3.91	3.93	3.95	3.97	3.99	4.01	4.03	4.04	4.06
60	3.59	3.64	3.68	3.72	3.75	3.78	3.81	3.83	3.86	3.88	3.90	3.92	3.93	3.95	3.97	3.98	4.00
70	3.56	3.61	3.65	3.69	3.72	3.75	3.78	3.80	3.82	3.84	3.86	3.88	3.90	3.91	3.93	3.95	3.96
80	3.54	3.59	3.63	3.67	3.70	3.73	3.75	3.78	3.80	3.82	3.84	3.86	3.88	3.90	3.91	3.93	3.95
90	3.53	3.57	3.61	3.65	3.68	3.71	3.73	3.76	3.78	3.80	3.82	3.84	3.85	3.87	3.89	3.90	3.92
100	3.51	3.56	3.60	3.63	3.66	3.69	3.72	3.74	3.76	3.78	3.80	3.82	3.83	3.85	3.87	3.88	3.90

Factor = $(n+1.1+n/4)$

(We are grateful to an anonymous reviewer for suggesting this approach.) In the methods previously described, nondetects are assigned a value of zero. This is not strictly correct. Values below a method detection limit represent *censored* or missing data We know the proportion of the sample that is missing, but we do not really know that their values are zero. Methods for estimating the mean of the Poisson distribution when the sample is restricted, as in the case of method detection limits, may also prove useful in the analysis of volatile organic data.

ACKNOWLEDGMENTS

The work reported herein was funded by a grant from Waste Management Incorporated. Waste Management also provided access to an extensive [illegible] data base that proved to be critical in the

ATTACHMENT GW-1

GROUNDWATER PARAMETER LIST

* References and citations made to specific sections, tables, figures or other sources which are not included in this Attachment are available in BFI's revised Post-Closure Permit application, dated May, 1989 and is in the Administrative Record. The Administrative Record is located at U. S. Environmental Protection Agency, Region II, Permits Administration Branch, 26 Federal Plaza, New York, N.Y., 10278 and the Puerto Rico Environmental Quality Board, Santurce, Puerto Rico, 00910-1488.

ATTACHMENT G.W.1

Priority Pollutant Volatile Parameters

Compound

Acrolein
Acrylonitrile
Benzene
bis (Chloromethyl) ether
Bromoform
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
2-Chloroethylvinyl ether
Chloroform
Dichlorobromomethane
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethylene
1,2-Dichloropropane
cis-1,3-Dichloropropylene
Ethylbenzene
Methyl bromide
Methyl chloride
Methylene chloride
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Toluene
1,2-Trans-dichloroethylene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethylene
Trichlorofluoromethane
Vinyl Chloride

Priority Pollutant Acid Parameters

2-Chlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
4,6-Dinitro-o-cresol
2,4-Dinitrophenol
2-Nitrophenol
4-Nitrophenol
p-Chloro-m-cresol
Pentachlorophenol
Phenol
2,4,6-Trichlorophenol

Priority Pollutant Base Neutral Parameters

Acenaphthene
Acenaphthylene
Anthracene
Benzidine
Benzo(a)anthracene
Benzo(a)pyrene
3,4-Benzofluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
bis (2-Chloroethoxy) methane
bis (2-Chloroethyl) ether
bis(2-Chloroisopropyl) ether
bis (2-Ethylhexyl) phthalate
4-Bromophenyl phenyl ether
Butyl benzyl phthalate
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Chrysene
Dibenzo (a,h) anthracene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
Diethyl phthalate
Dimethyl phthalate
Di-n-butyl phthalate
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
1,2-Diphenylhydrazine
Fluoranthene
Fluorene
Hexachlorobenzene
Hexachlorobutadien
Hexachlorocyclopentadiene
Hexachloroethane
Indeno (1,2,3-c,d) pyrene
Isophorone
Naphthalene
Nitrobenzene
N-Nitrosodimethylamine
N-Nitrosodi-n-propylamine
N-Nitrosodiphenylamine
Phenanthrene
Pyrene
1,2,4-Trichlorobenzene

Priority Pollutant Metals

Arsenic (As)
Cadmium (Cd)
Chromium (Cr)
Lead (Pb)
Mercury (Hg)
Selenium (Se)
Silver (Ag)
Antimony (Sb)
Beryllium (Be)
Copper (Cu)
Zinc (Zn)
Nickel (Ni)
Thallium (Tl)

Miscellaneous Priority Pollutant Parameter

Total Cyanide

Non-Priority Pollutant Parameters

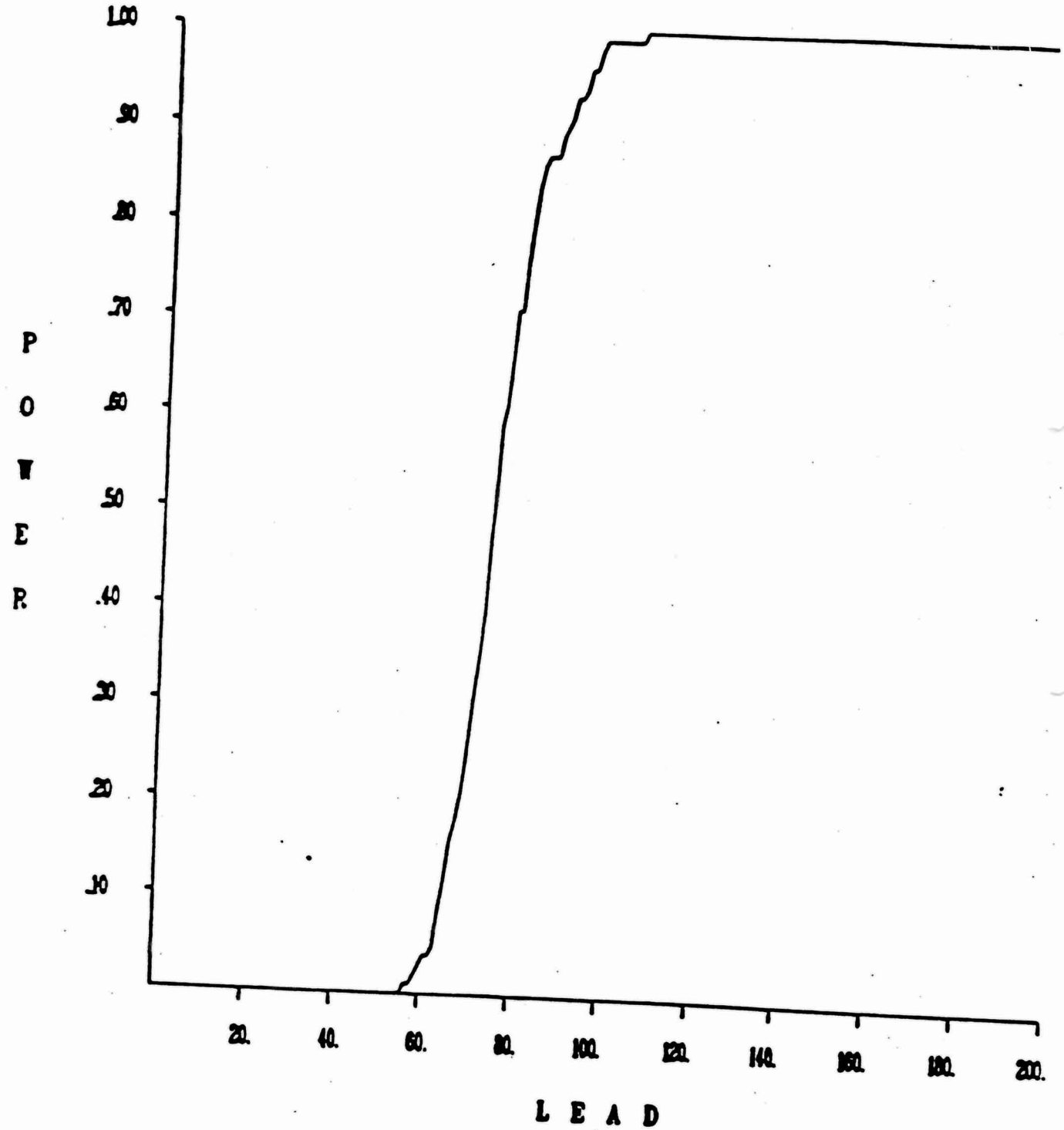
Specific Conductance (field value) (unfiltered)
Iron Total (filtered)
pH (field value) (unfiltered)
Temperature (field value) (unfiltered)
Tot- ~~Free and Amendable~~ Cyanide (unfiltered)
pH unfiltered (lab)
Specific Conductance (lab value) (unfiltered)

Subtitle D Parameters*

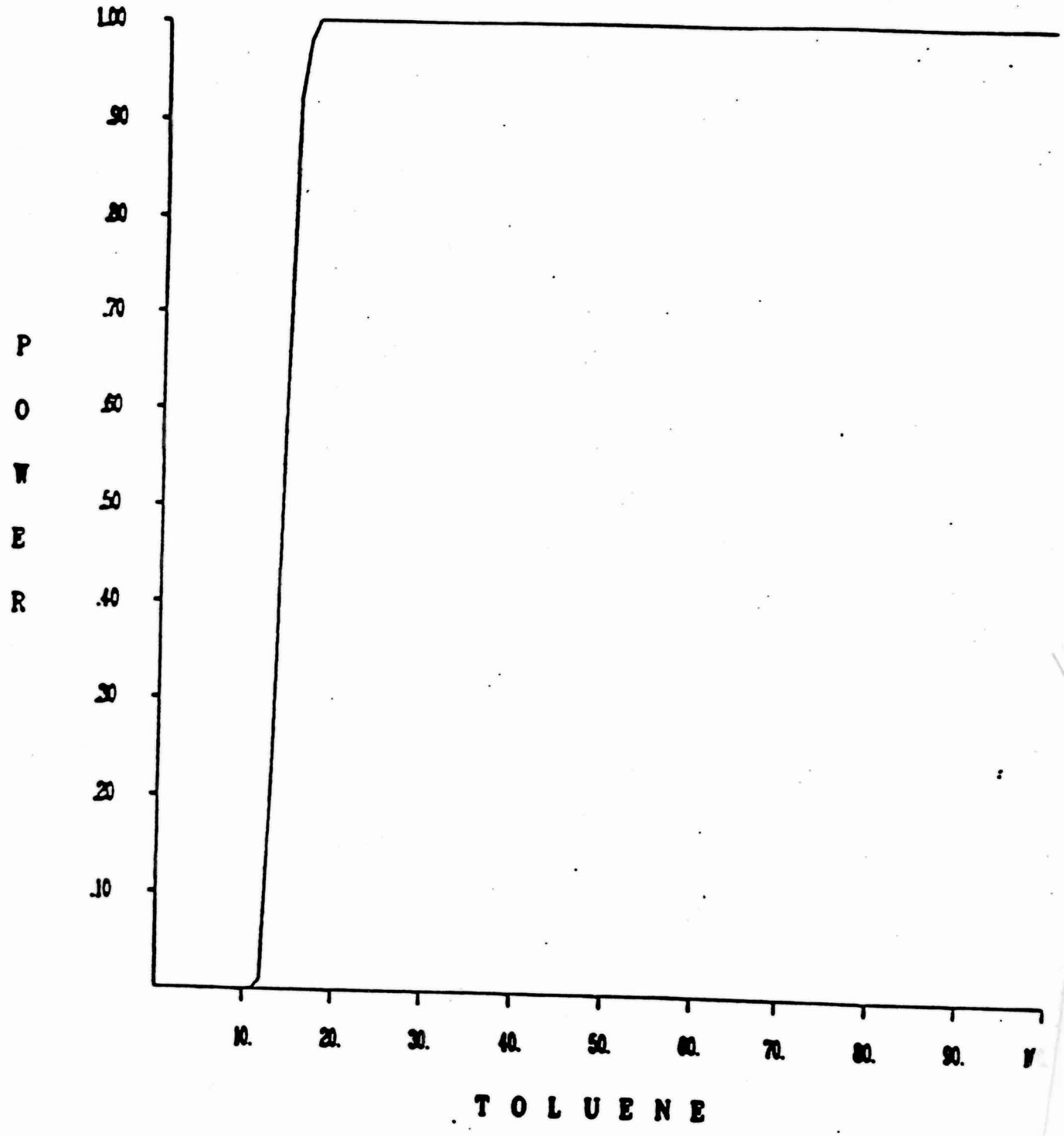
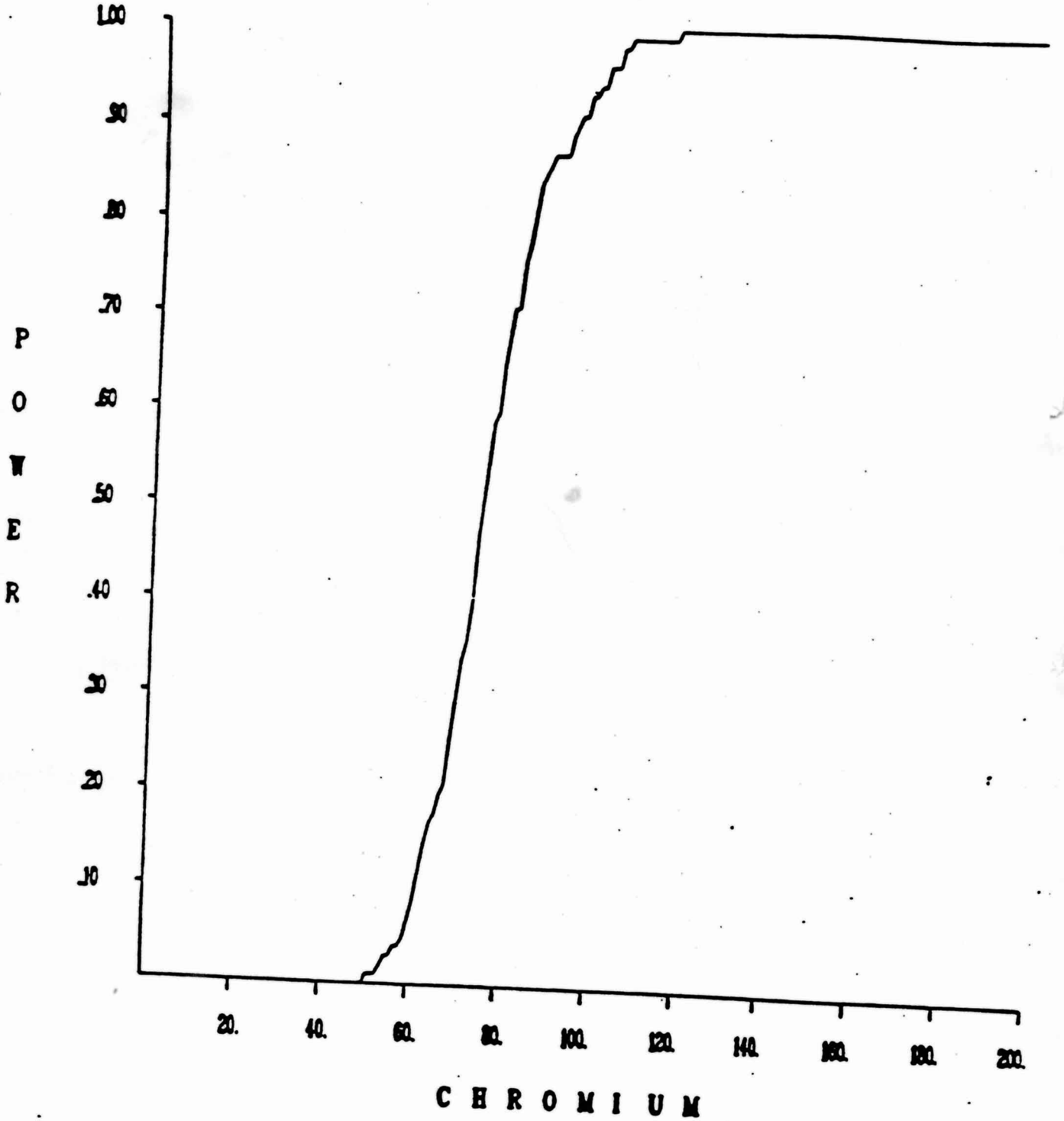
Acetone
Bromochloromethane
Trans-1,3-Dichloropropene
1,4-Difluorobenzene
Ethanol
Ethyl methacrylate
4-Bromofluorobenzene
Bromoform
2-Butanone (MEK)
Carbon disulfide
Dibromomethane
Chlorodibromomethane
1,4-Dichloro-2-butane
2-Hexanone
Iodomethane
4-Methyl-2-pentanone
Styrene
1,2,3-Trichloropropane
Vinyl acetate
Xylene
Barium
Cyanide

*Parameters also may appear on the Priority Pollutant List.

BACKGROUND N = 16, MEAN = 31.3 SD = 17.04 (K=4)



BACKGROUND N = 16, K = 4, MEAN = 6.875 UG/L



BACKGROUND N = 16, MEAN = 16.8[illegible], SD = 22.98 (K=4)